

# Mathematical Conception of “Phenomenological” Equilibrium Thermodynamics

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## Abstract

In the paper, the principal aspects of the mathematical theory of equilibrium thermodynamics are distinguished. It is proved that the points of degeneration of a Bose gas of fractal dimension in the momentum space coincide with critical points of real gases, whereas the jumps of critical indices and the Maxwell rule are related to the tunnel generalization of thermodynamics. Semiclassical methods are considered for the tunnel generalization of thermodynamics and also for the second and ultrasecond quantization (operators of creation and annihilation of pairs). To every pure gas there corresponds a new critical point of the limit negative pressure below which the liquid passes to a dispersed state (a foam). Relations for critical points of a homogeneous mixture of pure gases are given in dependence on the concentration of gases.

”Leontii Sergeevich wrote a play himself!”

”What for?” asked Natalya Ivanovna with apprehension,

”Are we running out of plays? Such good plays around.

And so many...”

”Leontii wrote a modern play!”

Here the old lady became quite alarmed.

”We do not start mutinies against the authorities!”

*M. Bulgakov “Theatrical Novel”*

## 1 Introduction

In his famous book on thermodynamics [1], Leontovich refers to thermodynamics as a phenomenological science, i.e., based on a series of “statements established experimentally”. Beginning with the creation of satellites and experiments in the absence of the gravity field of Earth, a new period in physical experimental investigations of thermodynamical phenomena occurred. Although these experiments are carried out by robots, and they cannot react like a human being to any situation and to change the parameters of the experiment like an animate observer, this must nevertheless unavoidably lead to a reconsideration of the original conception of the great physicists.

On the other hand, computer-aided experiments have been developed so greatly that a new science arose, the so-called molecular dynamics.

The problem of the mathematical axiomatization of thermodynamics and probability theory was posed already by Hilbert.

Already Poincaré gave the standard definition of probability as the ratio of the number of cases favorable for the event to the total number of possible events<sup>1</sup> and gave a counterexample to this definition of probability. This definition must be completed, writes Poincaré, by the sentence “under the assumption that these cases are equiprobable” ([2], Russian p. 116) and notes that we have completed a vicious circle place by defining probability via probability.<sup>2</sup>

After this, Poincaré writes: “The conclusion which seems to follow from this<sup>3</sup> is that the calculus of probabilities is a useless science, that the obscure instinct which we call common sense, and to which we appeal for the legitimisation of our conventions, must be distrusted.” ([2], Russian p. 116).<sup>4</sup>

Thus, first of all, the problem is to define what cases can be most naturally assumed to be equiprobable. “We are to look for a mathematical thought,” writes Poincaré, “where is remains pure, i.e., in arithmetic” ([24], Russian p. 14).<sup>5</sup>

The relationship between the quantum statistics of Bose gas with number theory (“arithmetics”) was traced by Vershik, one of the greatest contemporary mathematicians, who followed Temperley, a famous physicist [3]. Meanwhile, Poincaré notes that one still cannot reject probability theory, because probability theory is related to thermodynamics, and thermodynamics to experiment.

The author had to study the modern experiments in the most thorough way and profited from consultations with the great Russian virtuosi in experimental physics, including V. V. Brazhkin, K. I. Shmulovich, A. A. Vasserman, V. I. Nedostup, V. G. Baidakov, A. E. Gekhman, and also V. A. Istomin, the greatest expert in applied thermodynamics and the theory of gas mixtures. It was necessary to study the works of Professor D. I. Ivanov especially thoroughly; Professor Ivanov discovered a discrepancy between the Widom–Kadanoff–Wilson theoretical critical exponents ([4], [5], [6]) with the experimental ones ([7], [8]) and carried out classical measurements in thermodynamics.

Birkhoff, a great mathematician, devoted the first chapter of his book “Hydrodynamics” to paradoxes in hydrodynamics. In the strict mathematical understanding, a paradox is a counterexample to a system of axioms.

First of all, the system of axioms we have constructed includes a modified analog of the “equidistribution law” [9].

Our main axiom is the second one, which claims the (almost) uniform distribution of densities in a vessel. This axiom leads to number theory, where, instead of presenting all the theorems, we address the intuition of the physicists who are acquainted with the Bose–Einstein distribution (this distribution is closely related to number theory). This is sufficient for a new conception of the notion of ideal gas. Further we use the third axiom, claiming the existence of the Zeno-line for pure gases, which enables us to pass from ideal gases to unperfect ones. To explain the Maxwell rule and the jumps of critical indices at a critical point, as compared with the classical ones, we use the axiom of tunnel

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<sup>1</sup>“La définition, dira-t-on, est bien simple: la probabilité d’un événement est le rapport du nombre de cas favorables à cet événement au nombre total des cas possibles.”

<sup>2</sup>“On est donc réduit à compléter cette définition en disant: ‘... au nombre des cas possibles, pourvu que ces cas soient également probables.’ Nous voilà donc réduits à définir le probable par le probable.”

<sup>3</sup>Poincaré presents a series of contradictions in probability theory, including Bertrand’s paradox.

<sup>4</sup>“La conclusion qui semble résulter de tout cela, c’est que le calcul des probabilités est une science vaine, qu’il faut se défier de cet instinct obscur que nous nommions bon sens et auquel nous demandions de légitimer nos conventions.”

<sup>5</sup>“Il nous faut chercher la pensée mathématique là où elle est restée pure, c’est-à-dire en arithmétique.”

quantization of the classical equation of state, which thus encloses the system of four axioms.

The theory of ideal liquid treated as an incompressible one is a certain new model in equilibrium thermodynamics.

## 2 Heuristic considerations.

### The role of small viscosity

Following Clausius, experts in molecular physics usually argue by proceeding from the symmetry of the motion of a molecule averaged in all six directions. In the scattering problem, we use the principle of symmetry in all directions, which is standard in molecular physics, but apply it to define not the mean free path, but other molecular physics quantities. Therefore, the fraction of all particles that moves head-on is  $1/12$ . There are three such directions; hence, one quarter of all molecules collide<sup>6</sup>.

For the interaction potential, we consider the Lennard–Jones potential

$$u(r) = 4\varepsilon \left( \frac{a^{12}}{r^{12}} - \frac{a^6}{r^6} \right), \quad (1)$$

where  $\varepsilon$  is the energy of the depth of the well and  $a$  is the effective radius.

In the absence of an external potential, the two-particle problem reduces to the one-dimensional radial-symmetric one. As is well known [10], two quantities: the energy  $E$  and the momentum  $M$  are conserved in this problem. In the scattering problem, it is convenient to consider, instead of the momentum  $M$ , another preserved constant, namely,  $b = \sqrt{m}\rho$ , where  $\rho$  is the impact parameter, in such a way that

$$M = \sqrt{Eb}. \quad (2)$$

By solving with respect to energy  $E$  the well-known relation

$$E = \frac{p^2}{m} + \frac{M^2}{2mr^2} + u(r), \quad (3)$$

we obtain the attracting Hamiltonian  $H$ :

$$H = \frac{p^2/(2m) + u(r)}{1 - b^2/r^2}, \quad a < r \leq b. \quad (4)$$

The repulsing Hamiltonian is separated from  $H$  by a barrier. Repulsive particles put obstacles in the way of particles of the Hamiltonian  $H$ , by creating “viscosity”.

As the temperature decreases, the barrier height increases up to the value  $E_{\text{cr}} = 0.286\varepsilon$ , and then starts decreasing (see Fig. 1). According to rough energy estimates [11], for lesser temperatures, an additional barrier must arise when clusters form. This barrier can be given for carbon dioxide gas by micelles and for neutral gases and methane by germs of droplets, i.e., three-dimensional clusters that contain at least one molecule surrounded by other molecules (a prototype of a droplet)<sup>7</sup>.

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<sup>6</sup>The arguments put forward Clausius concerning symmetry which were applied by Clausius to evaluate the free path length and repeated here by the author are quite approximate. However, these arguments do not influence on the values of ratios of the form  $T_B/T_{\text{cr}}$ .

<sup>7</sup>By a “barrier” we mean an obstacle for the collision of particles, namely, an “envelope” of surrounding particles that defends the given particle from an immediate blow. In mathematics, a domain is an open region containing at least one point.

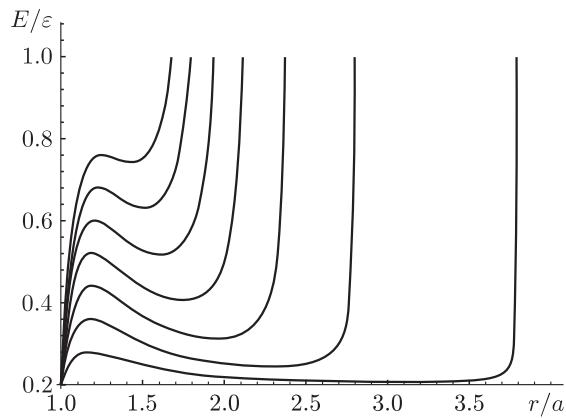


Figure 1: The values of  $E(b, r)$  for diverse values of the target parameter.

However, to study the penetration through the barrier of the incident particle, we must plot  $E$  along the  $y$  axis and turn the wells upside down. Then the minimum becomes the barrier and the maximum becomes the depth of the well.

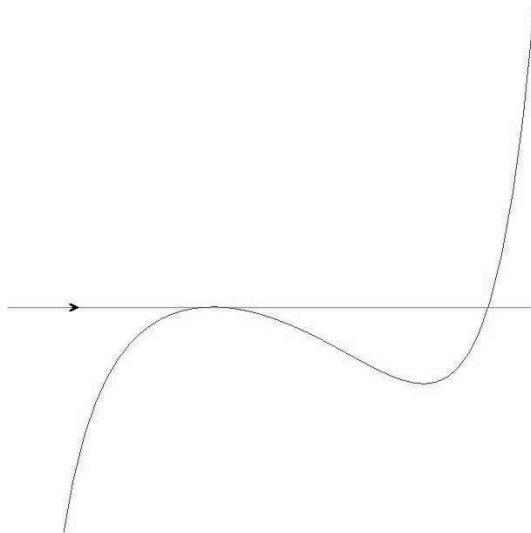


Figure 2: The trap for a fictitious particle in the the center of mass coordinate system. The radius vector  $r$  of the  $\mu$ -point is marked on the abscissa axis. The particle falls from the left from the point  $r = \rho$ , where  $\rho$  stands for the target parameter. In the original problem (1) (before the change of variables  $M = \sqrt{E}b$ ) the relation  $r = \rho$  is attained as  $r \rightarrow \infty$ .

A dimer can be formed in a classical domain if the scattering pair has an energy equal to the barrier height, slipping into the dip in “infinite” time and getting stuck in it as a result of viscosity (and hence of some small energy loss), because this pair of particles, having lost energy, hits the barrier on the return path. If the pair of particles has passed above this point, then the viscosity may be insufficient for the pair to become stuck: such a pair returns above the barrier after reflection. Therefore, only the existence of a point  $E = E_{\max}$  plus an infinitesimal quantity, where  $E_{\max}$  is the upper barrier point, is a necessary condition for the pair to be stuck inside the dip;  $E_{\max}^{\text{cr}}$  is the height of the maximum barrier.

We can compare the values  $T_{\text{cr}}$  with the values  $E_{\text{max}}^{\text{cr}}$  in the table below.

Substance	$\varepsilon, K$	$T_{\text{cr}}/4$	$E_{\text{cr}} \cdot \varepsilon/k$
<i>Ne</i>	36.3	11	10.5
<i>Ar</i>	119.3	37	35
<i>Kr</i>	171	52	50
<i>N<sub>2</sub></i>	95.9	31	28
<i>CH<sub>4</sub></i>	148.2	47	43

Above the value  $E_B = 0.8\varepsilon$ , the trap disappears. At the value  $0.286\varepsilon$ , the depth of the trap is maximum and corresponds to  $T_{\text{cr}} = \frac{1.16\varepsilon}{k}$ . For neon and krypton, as can be seen from the table, the concurrence is sufficiently good. Because  $T_B = 3.2\varepsilon/k$ , it follows that  $T_B/T_{\text{cr}} = 2.7$ , which corresponds to the known relation of “the law of corresponding states” [12].

The temperature corresponding to  $4E_B/k$ , is the temperature above which dimers do not appear. Exactly this is what we call the Boyle temperature (in contrast to [9]).

In fact, an application of the Clausius approach to the pairwise interaction gives a pairwise interaction with respect to the Lennard–Jones potential for two Gibbs ensembles of noninteracting molecules. This leads to the presence of a small friction for a single pair.

The difference  $E_{\text{max}} - E_{\text{min}}$  is equal to the energy needed for a particle lying at the bottom of the potential well to overcome the barrier. The value  $E_{\text{max}}$  corresponds to the temperature given by  $E_{\text{max}} = RT$ , where  $R$  stands for the universal gas constant. According to graph 2,  $E_{\text{min}}$  corresponds to the energy  $PV$ . Therefore,  $E_{\text{min}}/E_{\text{max}} \leq 1$  is the compressibility factor,  $Z = PV/RT$ . The temperature at the point  $E_{\text{min}} = E_{\text{max}}$  is equal to the Boyle temperature.

The dressed or “thermal” potential  $\varphi(r)$  is attractive [13]. In addition, because the volume  $V$  is a large parameter, it follows that, if the quantity  $\varphi(r) = (N\varepsilon a/\sqrt[3]{V})U(r/\sqrt[3]{V})$ , where  $U(r/\sqrt[3]{V})$  is a smooth function and  $N$  stands for the number of particles, is expanded in terms of  $1/\sqrt[3]{V}$ , then

$$U\left(\frac{r}{\sqrt[3]{V}}\right) = C_1 + \frac{C_2 r}{\sqrt[3]{V}} + \frac{C_3 r^2}{(\sqrt[3]{V})^2} + O\left(\frac{1}{(\sqrt[3]{V})^3}\right). \quad (5)$$

Expanding

$$C_1 + r^2 = \frac{(r - r_0)^2}{2} + \frac{(r + r_0)^2}{2}, \quad (6)$$

where  $C_1 = r_0^2$ , we can, just as in [13], separate the variables in the two-particle problem and obtain the scattering problem for pairs of particles and the problem of their cooperative motion for  $r_1 + r_2$ . The term  $C_2 r/\sqrt[3]{V}$  does not depend on this problem and the correction  $(a\varepsilon/\sqrt[3]{V})NO(1/V)$  is small.

Then, in the scattering problem, an attractive quadratic potential (inverted parabola multiplied by the density or, to be more precise, by the concentration, which we denote by the symbol  $\rho$  as well, because the target parameter does not occur below) is added to the Lennard–Jones interaction potential.

For this problem, we can find just as in (3)–(4), for all  $\rho = N/V$ , a point corresponding to the temperature at which the well capturing the dimers vanishes, and thus determine the so-called Zeno-line. It is actually a straight line (up to 2%), on which  $Z = E_{\text{min}}/E_{\text{max}} = 1$  (i.e., an ideal curve).

Let us clarify this fact in more detail.

We can treat the repulsing potential as a potential creating a small viscosity.  
Let us find the total energy of the attracting Hamiltonian,

$$E = \left( \frac{mv^2}{2(1 - b^2/r^2)} \right) + \frac{\Phi(r)}{1 - b^2/r^2}, \quad \Phi(r) = u(r) - \rho r^2.$$

The first term is negative for  $r \leq b$  and the other term is positive for  $b > r > a$  (i.e., the more is the speed, the less is energy). The mean speed is temperature.

Let us make the change of variables

$$\frac{r}{a} = r', \quad \frac{b}{a} = \tilde{b},$$

and get rid of  $a$ . In what follows, we omit both the tilde and the prime.

For a given  $b$ , the minimum  $r_1$  and the maximum  $r_2$  (see the graph no. 1 in [14]) are defined by the relation

$$\frac{dE}{dr} = 0. \quad (7)$$

This gives  $E_{\max}$  and  $E_{\min}$ . These values coincide at some point  $b = b_0$ , and hence

$$\frac{d^2 E}{dr^2} = 0 \quad (8)$$

at the point  $r_0$ , i.e.,  $E_{\max} = E_{\min}$ , and this is the very Zeno-line.

Let us construct the curve  $Z_{\min} = E_{\min}/E_{\max}$  minimal with respect to the target parameter as a function of  $\rho$ . Let us find the point  $Z = E_{\min}/E_{\max}$  for  $E_{\max} = E_{\max}^{\text{cr}}$  and find the corresponding point on the curve  $Z_{\min}(\rho)$ . This point is equal to  $Z_{\text{cr}} = 0.29$ , i.e., to the critical value of the compressibility factor  $Z$  for argon.

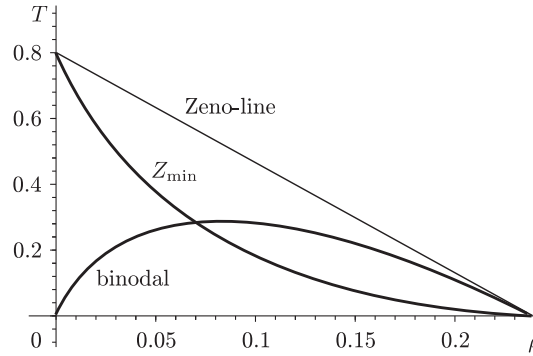


Figure 3: The binodal, the Zeno-line, and the curve  $Z_{\min}$ . This heuristic binodal does not coincide with the experimental one, whereas the Zeno-line and  $Z_{\text{cr}}$  are close to the corresponding experimental curves.

In order to obtain a binodal according to some “heuristic principle,” we must subtract the curve  $Z_{\min}(\rho)$  [15] from the Zeno-line. This gives the graph shown in Fig 3.

### 3 Quantum case

In an example describing the creation of a dimer, it is shown that, for  $T = T_c$ , one degree of freedom becomes “frozen”, and we obtain two degrees of freedom rather than three.

For a dimer with  $T > T_c$ , if the oscillational degrees of freedom are taken into account, then the number of degrees of freedom becomes equal to 6. Two degrees of freedom are obtained under the assumption that the oscillational degrees of freedom of the dimer are also “frozen” at  $T = T_c$ . If we suppose this heuristic supposition for the quantum case, then, for  $T < T_d$ , both dimers with two degrees of freedom and dimers with six degrees of freedom are created. This corresponds to the two-liquid Thiess–Landau model [67]. In this case, the dimers with two degrees of freedom give the  $\lambda$ -point and the dimers with six degrees of freedom give superfluidity. Indeed, in the two-dimensional case we have

$$c_p \cong \frac{2T}{T_d} \int_0^\infty \frac{\xi d\xi}{e^\xi - 1} + \frac{T}{T_d} \int_0^\infty \frac{e^\xi \xi d\xi}{(e^{\xi - \mu/T} - 1)^2} + O\left(\frac{T - T_d}{T_d}\right),$$

and we obtain a logarithmic divergence at the point  $\xi = 0$  for  $\mu \rightarrow 0$ .

The case in which  $N$  is not so large as it is in statistical physics, i.e., the so-called mesoscopic state (see [68]), can also be of interest for us. In this case, let us use Fock’s idea for the Hartree equations, which lead to the Hartree–Fock equations, which agree well with experiments for a not too large number of electrons in atoms.

Namely, we consider the single-particle equation of the mean field (a self-consistent field) and apply (to the resulting “dressed” potential) the procedure of transition to the  $N$ -partial Schrödinger equation with a dressed potential, just as we proceeded above for the operator  $\frac{\hbar^2}{2m}\Delta$ . Here we can consider two ways of investigation. The first way is the way used by Fock and which leads in the semiclassical limit to the Thomas–Fermi equations for the dressed potential. Another way is to consider the Hartree temperature equations (see [69]) and to obtain the Thomas–Fermi temperature equations in the classical limit.

Since the quantity  $T_d$  is small, it is easier to use the first way and to find the “dressed” potential.

Let  $V(q - q')$  be a pairwise interaction potential such that  $\int |V(r)| dr < \infty$ . The dressed potential  $W(q)$  is given by the formula

$$W(q) = U(q) + \int V(q - q') |\psi(q')|^2 dq',$$

where  $U(q)$  stands for the external potential and  $\psi(q')$  for an eigenfunction of the Schrödinger equation which depends on the “dressed” potential and is thus an equation with a “unitary” nonlinearity. The expansion of the equation in powers of  $\hbar$  can be found by the method of complex germ up to  $O(\hbar^k)$ , where  $k$  is an arbitrarily large number<sup>8</sup> (see [69], where system (63) defines a complex germ; see also [40], [75–80]).

Further, we consider two asymptotic formulas for the number of eigenvalues of the one-particle Schrödinger operator.

The  $2D$ -dimensional phase space is partitioned into a lattice, and the number  $G_j$  is determined by the formula

$$G_i = \frac{\Delta p_j \Delta q_j}{(2\pi\hbar)^D}. \quad (9)$$

This relation was obtained by Weyl.

In the mathematical literature, the same notion for the number of eigenvalues of the Laplace operator with the Dirichlet conditions on the boundary of a  $D$ -dimensional

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<sup>8</sup>For  $U(q) \equiv 0$ , one obtains Bogolyubov’s famous equation [70]. The creation of dimers leads to the ultrasecond quantization, i.e., to the operators of creation and annihilation of pairs. This makes it possible to satisfy the boundary conditions in a capillary (46–48, 71–73).

volume, which are less or equal to a given  $\lambda$ , is called the Courant formula:

$$\rho(\lambda) = \frac{Vm^{D/2}\lambda^{D/2}}{\Gamma(D/2+1)(2\pi)^{D/2}h^D}(1+o(1)) \quad \text{as } \lambda \rightarrow \infty, \quad (10)$$

where  $D$  stands for the dimension of the space, because the spectral density has the asymptotic behavior.

The asymptotics

$$\lambda_j \sim \frac{2h^2}{m} \left( \frac{\pi^{D/2}\Gamma(D/2+1)}{V} \right)^{2/D} j^{2/D} \quad \text{as } j \rightarrow \infty, \quad (11)$$

is a natural generalization of formula (10).

To reconcile the notion of Bose statistics which is given in [9] with symmetric solutions of the  $N$ -particle Schrödinger equation, i.e., of the direct sum of  $N$  noninteracting Hamiltonians corresponding to the Schrödinger equation, and the symmetric solutions of their spectrum, it is more appropriate to assign to the cells the multiplicities of the spectrum of the Schrödinger equation in the way described in [81].

Consider the nonrelativistic case in which the Hamiltonian  $H$  is equal to  $p^2/(2m)$ , where  $p$  stands for the momentum.

The comparison of  $G_i$  with the multiplicities of the spectrum of the Schrödinger equation gives a correspondence between the eigenfunctions of the  $N$ -particle Schrödinger equation that are symmetric with respect to the permutations of particles and the combinatorial calculations of the Bose statistics that are presented in [9].

A single-particle  $\psi$ -function satisfies the free Schrodinger equation with the Dirichlet conditions on the vessel walls.

Using precisely this very correspondence, we establish a relationship between the Bose-Einstein combinatorics [9], the definition of the  $N$ -particle Schrödinger equation, and the multiplicity of the spectrum of the single-particle Schrödinger equation.

The spectrum of the single-particle Schrödinger equation, provided that the interaction potential is not taken into account, coincides, up to a factor, with the spectrum of the Laplace operator. Consider its spectrum for the closed interval, for the square, and for the  $D$ -dimensional cube with zero boundary conditions. This spectrum obviously consists of the sum of one-dimensional spectra.

On the line we mark the points  $i = 0, 1, 2, \dots$  and on the coordinate axes  $x, y$  of the plane we mark the points with  $x = i = 0, 1, 2, \dots$  and  $y = j = 0, 1, 2, \dots$ . To this set of points  $(i, j)$  we assign the points on the line that are positive integers,  $l = 1, 2, \dots$ .

To every point we assign a pair of points,  $i$  and  $j$ , by the rule  $i + j = l$ . The number of these points is  $n_l = l + 1$ . This is the two-dimensional case.

Consider the 3-dimensional case. On the axis  $z$  we set  $k = 0, 1, 2, \dots$ , i.e., let

$$i + j + k = l$$

In this case, the number of points  $n_l$  is equal to

$$n_l = \frac{(l+1)(l+2)}{2}.$$

It can readily be seen, for the  $D$ -dimensional case, that the sequence of multiplicities for the number of variants  $i = \sum_{k=1}^D m_k$ , where  $m_k$  are arbitrary positive integers, is of the form

$$q_i(D) = \frac{(i+D-2)!}{(i-1)!(D-1)!}, \quad \text{for } D = 2, \quad q_i(2) = i, \quad (12)$$



$$\sum_{i=1}^{\infty} N_i = N, \quad \varepsilon \sum_{i=1}^{\infty} q_i(D) N_i = E. \quad (13)$$

The following problem in number theory corresponds to the three-dimensional case  $D = 3$  (cf. [9]):

$$\sum_{i=1}^{\infty} N_i = N, \quad \varepsilon \sum_{i=1}^{\infty} \frac{(i+2)!}{i!6} N_i = M, \quad M = \frac{E}{\varepsilon}. \quad (14)$$

In the manual [9], following Einstein, a passage to the limit is carried out as  $N \rightarrow \infty$ , which enables one to pass from sums to integrals. Then, in the section “Degenerate Bose gas,” a point is distinguished which corresponds to the energy equal to zero. This very point is the point of Bose condensate on which excessive particles whose number exceeds some value  $N_d \gg 1$  are accumulated at temperatures below the so-called degeneracy temperature  $T_d$ . The theoretical discovery of this point anticipated a number of experiments that confirmed this fact not only for liquid helium but also for a series of metals and even for hydrogen.

From a mathematical point of view, distinguishing a point in the integral is an incorrect operation if this point does not form a  $\delta$  function.

The author obtained a more precise expression for the Bose–Einstein but for finite values  $N_d \gg 1$  (see, e.g., [82]).

Thus, we consider the case in which  $N \gg 1$ , but  $n$  is not equal to infinity, on the physical level of rigor [82]. For the final parastatistics we have

$$n_j = \frac{1}{\exp\{\frac{\varepsilon_j - \mu}{T}\} - 1} - \frac{k+1}{\exp\{(k+1)\frac{\varepsilon_j - \mu}{T}\} - 1}, \quad n_j = \frac{N_j}{G_j}. \quad (15)$$

In our case, we have  $k = N_d$ , and the point of condensate is  $\varepsilon_0 = 0$ .

By (9), it is clear that  $G_j$  is associated with the  $D$ -dimensional Lebesgue measure and, in the limit with respect to the coordinates  $\Delta q_j$ , gives the volume  $V$  in the space of dimension 3 and the area  $Q$  in the space of dimension 2. The passage with respect to the momenta  $\Delta p_j$  is also valid as  $N \rightarrow \infty$  and  $\mu > \delta > 0$ , where  $\delta$  is arbitrarily small.

Expanding (15) at the point  $\varepsilon_0 = 0$  in the small parameter  $x = (\mu N_d)/T_d$ , where  $N_d$  stands for the number of particles corresponding to the degeneration and  $T_d$  for the degeneracy temperature, and writing  $\xi = -\mu/T_d$ , we obtain

$$\begin{aligned} n_0 &= \left\{ \frac{1}{\exp\{\frac{-\mu}{T}\} - 1} - \frac{N_d + 1}{\exp\{(N_d + 1)\frac{-\mu}{T}\} - 1} \right\} = \frac{e^{\xi N_d} - 1 - (N_d + 1)(e^{\xi} - 1)}{(e^{\xi} - 1)(e^{2N_d} - 1)} \\ &= \frac{N_d}{2} \frac{1 + \frac{x}{6} + \frac{x^2}{4!} + \frac{x^3}{5!} + \dots}{1 + \frac{x}{2} + \frac{x^2}{6} + \frac{x^3}{4!} + \dots} = \frac{N_d}{2} \left( 1 - \frac{x}{3} - \frac{11}{24}x^2 - 0.191x^3 - \dots \right). \end{aligned} \quad (16)$$

For example, if  $x \rightarrow 0$ , then  $n_0 = N_d/2$ , and hence the number  $n_0$  in the condensate at  $T = T_d$  does not exceed  $N_d/2$ . If  $x = 1.57$ , then  $n_0 \approx N_d/10$ . Certainly, this affects the degeneracy temperature, because this temperature can be expressed only in terms of the number of particles above the condensate,  $\tilde{N}_d$ , rather than in terms of the total number of particles  $N_d$  (which is equal to the sum of  $\tilde{N}_d$  and of the number of particles in the condensate).

Write  $M = E_d/\varepsilon_1$ , where  $\varepsilon_1$  stands for the coefficient in formula (11) for  $j = 1$ . Let us find  $E_d$ ,

$$E_d = \int_0^{\infty} \frac{\frac{|p|^2}{2m} d\varepsilon}{e^{\frac{|p|^2}{2m}/T_d} - 1}, \quad (17)$$

where

$$d\varepsilon = \frac{|p|^2}{2m} \frac{dp_1 \dots dp_D dV_D}{(2\pi\hbar)^D}. \quad (18)$$

Whence we obtain the coefficient  $\alpha$  in the formula,

$$E_d = \alpha T_d^{2+\gamma} \zeta(1 + D/2) \Gamma(1 + D/2). \quad (19)$$

To begin the summation in (13) at the zero index (beginning with the zero energy), it is necessary to rewrite the sums (13) in the form

$$\sum_{i=0}^{\infty} N_i = N, \quad \varepsilon \sum_{i=0}^{\infty} (q_i(D) - 1) N_i = E - \varepsilon N. \quad (20)$$

The relationship between the degeneracy temperature and the number  $\tilde{N}_d$  of particles above the condensate for  $\mu > \delta > 0$  (where  $\delta$  is arbitrarily small) can be found for  $D > 2$  in the standard way.

Thus, we have established a relationship between  $G_i$  in formula (9) (which is combinatorially statistical) and the multiplicity of the spectrum for the single-particle Schrödinger equation, i.e., between the statistical [9] and quantum-mechanical definitions of Bose particles.

Consider the two-dimensional case in more detail. There is an Erdős' theorem for a system of two Diophantine equations,

$$\sum_{i=1}^{\infty} N_i = N, \quad \sum_{i=1}^{\infty} i N_i = M. \quad (21)$$

The maximum number of solutions of this system is achieved if the following relation is satisfied:

$$N_d = c^{-1} M_d^{1/2} \log M_d + a M_d^{1/2} + o(M_d^{1/2}), \quad c = \pi\sqrt{2/3}, \quad (22)$$

and if the coefficient  $a$  is defined by the formula  $c/2 = e^{-ca/2}$ .

The decomposition of  $M_d$  into one summand gives only one version. The decomposition  $M_d$  into  $M_d$  summands also provides only one version (namely, the sum of ones). Therefore, somewhere in the interval must be at least one maximum of the variants. Erdős had evaluated it (22) (see [83]).

If the number  $N$  increases and  $M$  is preserved in the problem (21), then the number of solutions decreases. If the sums (21) are counted from zero rather than from one, i.e., if we set

$$\sum_{i=0}^{\infty} i N_i = (M - N), \quad \sum_{i=0}^{\infty} N_i = N, \quad (23)$$

then the number of solutions does not decrease and remains constant.

I shall try to explain this effect. The Erdős–Lehner problem [84] is to decompose  $M_d$  into  $N \leq N_d$  summands.

Let us expand the number 5 into two summands. We obtain  $3 + 2 = 4 + 1$ . The total number is 2 versions (this problem is known as “partitio numerorum”). If we include 0 to the possible summands, we obtain three versions:  $5 + 0 = 3 + 2 = 4 + 1$ . Thus, the inclusion of zero makes it possible to say that we expand a number into  $k \leq n$  summands. Indeed, the expansion of the number 5 into three summands includes all the previous versions, namely,  $5 + 0 + 0$ ,  $3 + 2 + 0$ , and  $4 + 1 + 0$ , and adds new versions, which do not include zero.

In this case, the maximum does not change drastically [84]; however, the number of versions is not changed, namely, the zeros, i.e., the Bose condensate, make it possible that the maximum remains constant, and the entropy never decreases; after reaching the maximum, it becomes constant.

Let us turn to a physical definition.

Note first that, without changing the accuracy of the quantity whose logarithm is evaluated, we can replace  $\log M_d$  by  $(1/2) \log(\tilde{N}_d/Q)$ . Then

$$\sqrt{M_d} = \frac{2\tilde{N}_d/Q}{c^{-1} \log(\tilde{N}_d/Q) + a} + o\left(\frac{\tilde{N}_d}{Q}\right). \quad (24)$$

In our case,  $\tilde{N}_d/Q$  corresponds to the number of particles above the condensate.

According to formula (19), in the two-dimensional case we must set  $\gamma = 0$  and find the coefficient  $\alpha$ . Then formula (24) gives us a relationship between  $\tilde{N}_d$  and  $T_d$  due to the fact that the number of particles in the condensate is  $o(\tilde{N}_d)$ .

In fact, we have proved that there is a gap between  $\mu > \delta > 0$  and  $\mu = 0$ .

## 4 Main axiom and theorem for the classical gas

Consider the Maxwell distribution

$$\omega(p) = \frac{1}{(2\pi mT)^{3/2}} \exp\left\{-\frac{p^2}{2mT}\right\}. \quad (25)$$

As is well known<sup>9</sup>, it is associated with the potential

$$\Omega = \frac{V\pi^{3/2}T^{5/2}m^{5/2}}{\Gamma(2+1/2)} \int_0^\infty t^{3/2} e^{-(t-\frac{\mu}{T})} dt. \quad (26)$$

Now consider an ultrarelativistic gas in which the kinetic energy is proportional to  $|p|$ . In this case,

$$\omega(p) = \frac{c^3}{(\pi T)^3} \exp\left\{-\frac{c|p|}{T}\right\}, \quad (27)$$

where  $c$  is the velocity of light. For this gas, the potential  $\Omega$  is of the form

$$\Omega = VT^3 \frac{\pi^2}{\Gamma(3)c^3} \int_0^\infty t^3 e^{-(t-\frac{\mu}{T})} dt. \quad (28)$$

Since  $N = -\frac{\partial\Omega}{\partial\mu}$  and  $P = -\frac{\partial\Omega}{\partial V}$ , it follows that, in both the first and the second case, we obtain the equation of an ideal gas

$$PV = NT. \quad (29)$$

In thermodynamics, there is an important notion, namely,  $l$ , the number of the degrees of freedom of the molecule. The energy of the molecule is

$$E \sim l \frac{p^2}{2m}.$$

---

<sup>9</sup>We have kept the integral especially without evaluating it.

The parameter  $l$  (the number of degrees of freedom) is the coefficient at the potential  $\Omega$ . It does not influence the equation of ideal gas (29). This coefficient is related to the so-called “equidistribution law” mentioned above. Possibly, the law is true in some interval of temperatures. However, as the temperature reduces, some degrees of freedom can be “frozen.” It turns out that it is much more convenient to introduce the parameter  $\sigma$  presented below.

Assuming that the value of  $l$  depends on the momentum, we replace the above relation by the following one:

$$E_\gamma = \frac{|p|^{2+\sigma}}{2mp_0^\sigma}, \quad (30)$$

where  $p_0$  stands for some typical momentum.

We can say that both the average momentum and the number of the degrees of freedom depend on the temperature, and hence the number of the degrees of freedom depends on the momentum. We assume that this dependence is the simplest one, namely, it is a power dependence (the parameter  $\sigma$  of in the exponent characterizes the molecule). Here the potential  $\Omega$  takes the form

$$\Omega_\gamma = \frac{\pi^{1+\gamma}}{\Lambda^{2(1+\gamma)}} VT^{2+\gamma} \frac{m^{2+\gamma}}{\Gamma(2+\gamma)} \int_0^\infty t^{1+\gamma} e^{-(t-\frac{\mu}{T})} dt, \quad (31)$$

$$\gamma = \frac{3}{2+\sigma} - 1 = \frac{1-\sigma}{2+\sigma},$$

where  $\Lambda$  stands for a constant corresponding to a given molecule and depending on its mass (however, we try to avoid the mass by passing from the density to the concentration). It can readily be seen that, in this case, relation (29) remains valid for an ideal gas.

Thus, we replace the parameter of the integer degrees of freedom by some continuous parameter that characterizes the given molecule. In principle, this parameter  $\gamma$  is of the same physical origin as the number of the degrees of freedom. But since it is continuous, it takes into account more details of the spectrum of the molecule.

Moreover, below we shall see the following remarkable fact: every molecule is characterized by its own value of  $\gamma$  which does not depend on temperature and depends only on the dimensionless value  $Z_{\text{cr}}$ , which is its critical compressibility factor.

One must not think that this relation (formula (30)) holds for a single molecule. It can be treated only as a result of averaging over the Gibbs ensemble of noninteracting molecules that corresponds to some temperature (as we shall see below, this ensemble corresponds to the critical temperature  $T_{\text{cr}}$ ).

Roughly speaking, the number of degrees of freedom is related to the number of atoms [9], whereas the number of atoms is related to the dimension of the space. For this reason, the reduction of the number of degrees of freedom, as the temperature reduced, is equivalent in a Gibbs ensemble of noninteracting molecules to the reduction of the mean value of the space dimension. On the other hand, one can say that the reduction of the number of degrees of freedom is analogous to the reduction of the dimension of the space of oscillators (from three-dimensional to zero-dimensional oscillators), whereas the latter reduction is equivalent (see Sec. 5) to the halving of the dimension of the momentum space. However, for the value of the potential  $\Omega$ , increasing of the exponent of  $p$  in energy is equivalent to the reduction of the fractal dimension when integrating with respect to  $p$ . Therefore, the passage to  $E(p) = ap^\alpha$ , which is regarded as an equivalent notion of fractal dimension, is related to averaging of the Gibbs ensemble of noninteracting molecules with respect to the number of active degrees of freedom. Therefore, the formal

change of variable in manuals ([60], p. 212) and handbooks [61] (see the section “Integral representations” in [61] and also the book [62]) has a well-founded physical meaning of continuous reduction of a fractional value of the number of degrees of freedom of a molecule as the temperature reduces (in the mean) for a Gibbs ensemble of noninteracting molecules.

A. V. Chaplik suggested another interpretation of this law. Since it turns out that a law of the form  $ap^\alpha$  enables us to describe the experiment, and since we assume that this is an ideal gas of particles with this dependence,  $E(p) = ap^\alpha$ , it follows that these are quasiparticles, i.e., collective excitements (rather than individual molecules). The  $p$ -momentum of the quasiparticle is preserved, because the interaction between the particles is no longer valid. This trick is customary in physics.

However, in mathematics, the notion of Gibbs ensemble corresponds to the notion of the Kolmogorov complexity, and therefore, for a mathematician, it is more natural to relate the formula  $E(p) = ap^\alpha$  to this vary complexity. However, the main point is that this generalizes the notion of equidistribution to lower temperatures.

Now we can rigorously formulate the axiom of thermodynamics corresponding to the approximate conservation of the gas density (this corresponds to the physicists’ statement in equilibrium thermodynamics: “the density is homogeneous in a vessel”; physicists consider equilibrium thermodynamics as a separate discipline, after which fluctuation theory is also considered separately).

A physicist thinks that the density of particles inside the vessel is constant up to fluctuations (of the order of the square root of the number of particles in a small subvolume). This means that the physicist counts the number of particles in every small subvolume containing approximately one million of particles, and the density does not depend on the permutation of the numbers of particles. However, this is arithmetics, in which the sum does not depend on the permutation of summands (in contrast to the Boltzmann statistics in which a permutation of particles gives a new state). Even if we assume that the experimenter had indexed all particles during the previous measurement, this experimenter cannot control what index corresponds to a given particle at the next moment of measurement, and the indexing can be carried out again to compute the density. This is a fact in arithmetics, which is the very base of a special branch of science, namely, of analytic number theory.

**Main mathematical axiom of thermodynamics.** *Consider a vessel of volume  $V$  containing  $N > 10^{19}$  identical molecules corresponding to the parameter  $\gamma = \gamma_0$ . Consider a small convex volume of size  $V_\delta$  containing  $N_\delta$  particles, where  $N_\delta$  is not less than  $10^6$ . Let  $\mathbb{P}$  be the probability of the deviation*

$$N_\delta \pm \sqrt{N_\delta}$$

*for any volume of size  $V_\delta$  inside the vessel. The claim of the axiom is that the probability  $\mathbb{P}$  is sufficiently small. Namely,*

$$\mathbb{P}\left\{\left|\frac{N}{V} - \frac{N_\delta}{V_\delta}\right| > \frac{\sqrt{N_\delta}}{V_\delta}\right\} \leq \frac{0.01}{\sqrt{\log N_\delta}}. \quad (32)$$

This implies that the numbering of particles in the volume  $V_\delta$  is arbitrary and does not affect the density. We can rearrange the numbers, and this also does not affect the density, because the rearrangement of summands does not change the sum<sup>10</sup>.

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<sup>10</sup>The set of initial data for an  $N$ -particle dynamical system can be said to be chaotic if a relation of the form (32) arises at a sufficiently large time interval. The weakening of condition (32) does not influence the validity of relation (34).

*Remark 1.* Condition (32) shows that the theory presented below cannot be applied for insufficiently many particles. This condition also shows what is the accuracy that can be expected from the relations obtained below. The weakening of condition (32) plays no fundamental role, and is manifests itself only at the level of the expected accuracy of these relations.

Thus, we have already proved that the approximate conservation of density inside a gas volume implies that the particles are independent of the numbering, and hence are Bose particles. Therefore, the potential  $\Omega_\gamma$  (31) must be replaced by the Bose gas potential<sup>11</sup>,

$$\Omega_\gamma = \frac{\pi^{1+\gamma}}{\Lambda^{2(1+\gamma)}} VT^{2+\gamma} \frac{1}{\Gamma(2+\gamma)} \int_0^\infty \frac{t^{1+\gamma}}{e^{(t-\frac{\mu}{T})} - 1} dt = \frac{\pi^{1+\gamma}}{\Lambda^{2(1+\gamma)}} VT^{2+\gamma} \text{Li}_{\gamma+2}(e^{\mu/T}), \quad (33)$$

where  $\text{Li}_\gamma(\cdot)$  stands for the polylogarithm,  $\text{Li}_{\gamma+2}(1) = \zeta(\gamma+2)$ , and  $\zeta$  stands for the Riemann zeta function.

Thus, in our case, the Bose gas also depends on another parameter,  $\gamma$ . We refer to this parameter as the *fractional* (“*fractal*”) *dimension* in the momentum space (cf. [9], Sec. Degenerate Bose gas, footnote). the parameter could be called more precisely the *parameter characterizing the spectrum of the molecule*.

*Remark 2.* In the statistics of Boltzmann, Shannon, and Kolmogorov,  $4+1$  and  $1+4$  are different variants. In arithmetic, they constitute one variant. For  $\gamma > 0$ , the Bose statistics is related to number theory. In the physical literature, this was first noted by Temperley [3]; in the mathematical literature, this was considered in detail in [16]–[18].

*Remark 3.* Note that, just as for the standard potential  $\Omega_\gamma$  (31), three-dimensional Bose gas corresponds to  $\gamma = 1/2$ , whereas  $\gamma = 2$  corresponds to ultrarelativistic gas. The latter is associated with the famous Planck distribution at  $\mu = 0$  for the black-body radiation (cf. [9], Sec. 60).

**Theorem 1.** *The point of degeneracy of the Bose distribution at  $\mu = 0$  for molecules of characteristic  $\gamma$  coincides with the critical points of these molecules up to normalization. Therefore, the dimensionless quantity*

$$Z_{\text{cr}} = \frac{V_{\text{cr}} P_{\text{cr}}}{RT_{\text{cr}}},$$

*where  $R$  stands for the gas constant, coincides with the dimensionless point of degeneracy of an ideal Bose gas of fractal characteristic  $\gamma$ . Hence,*

$$Z_{\text{cr}} = \left( \frac{V}{T} \frac{\partial \Omega_\gamma}{\partial V} \right)_{\mu=0} \bigg/ \left( \frac{\partial \Omega_\gamma}{\partial \mu} \right)_{\mu=0} = \frac{\zeta(\gamma+2)}{\zeta(\gamma+1)}, \quad (34)$$

*which is a consequence of the number-theoretic interpretation of the Bose distribution.*

This is a property of the new ideal gas without interaction. Apfelbaum and Vorob’ev [19] computed the critical isotherms in the  $\{P, V\}$ -plane for different gases, where the value of  $\gamma$  is determined by the above formula, and the critical isotherm of the Bose gas with the evaluated characteristic  $\gamma$  was computed by the relevant formulas for an ideal Bose gas<sup>12</sup> (see Figs. 4–5).

<sup>11</sup>The Bose gas is usually regarded as a quantum gas; however, it is related to number theory (see Remark 2 below), and number theory is related to the main axiom. Therefore, the potential  $\Omega_\gamma$  (33) can be applied to classical gas. In number theory,  $V \equiv 1$ . To make the perception by the physicists more convenient, we keep the multiplier  $V$  (cf. (4)–(38) below).

<sup>12</sup>This gas is more general than that in [20] and corresponds to the fractal dimension  $\gamma$  in the momentum space. In [20],  $\gamma = 1/2$ . There is no classical gas of this dimension.

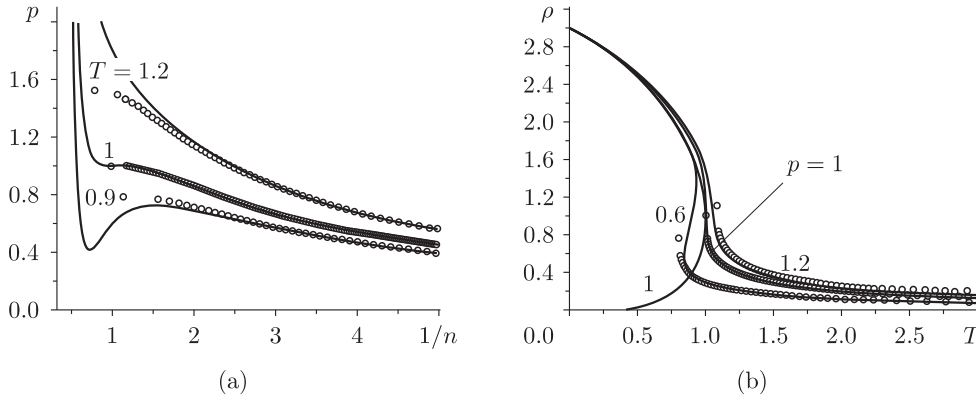


Figure 4: (a) Isotherms of pressure for the van der Waals equation are shown by continuous lines. The small circles show the corresponding lines computed with  $\gamma = 0.312$  for  $\varphi(V) = V$  (i.e., ideal Bose gas),  $Z_{\text{cr}} = 3/8$ .

(b) Isobars of density for the van der Waals equation are shown by continuous lines. Line 1 is the binodal curve. The small circles correspond to Bose-Einstein isobars for  $\gamma = 0.312$ .

At first glance, it looks as if the notion of new ideal gas leads to an alteration of the famous relation

$$PV = NT \quad (35)$$

(which, moreover, served as an analogy for the main economics law, the Irving Fisher formula; which is used to calculate the “turnover rate” of capital [21]). This would be surprising indeed. However, this is not the case. The relation  $PV = NT$  or, equivalently,  $PV = RT$  (because the number of particles in the vessel remains the same) defines an imperfect gas and, in contemporary experimental thermodynamical diagrams, it is called the *Zeno-line* or, sometimes, the ideal curve, the Bachinskii parabola, etc.

On the diagram  $(\rho, T)$  for pure gases, this is the straight line  $Z = 1$ . The line is a most important characteristic feature for a gas which is imperfect. Since, for imperfect gases, it has been calculated experimentally and is an “almost straight” line on the  $(\rho, T)$  diagram, it follows that the Zeno-line is determined by the two points  $T_B$  and  $\rho_B$  called the “Boyle temperature” and the “Boyle density.” In contrast to  $Z_{\text{cr}}$ , these points are related to the interaction and scattering of a pair of gas particles with the interaction potential peculiar to this gas, as was shown in Sec. 1 and in other papers of the author (see, e.g., [22]). Therefore, the Zeno-line on which the relations

$$PV = NT, \quad \frac{\rho}{\rho_B} + \frac{T}{T_B} = 1, \quad \frac{N}{V} = \rho, \quad (36)$$

are satisfied, where  $\rho$  is the density (the concentration), is a consequence of pairwise interaction, and thus is a relation for an imperfect gas.

The correction related to the existence of the Zeno-line leads to a differential equation [23] whose numerical solution yields an alteration to the gas spinodal for every particular pure gas. For argon and  $\text{CO}_2$ , this modification is shown in Fig. 6<sup>13</sup>.

<sup>13</sup>By the heuristic considerations related to the scattering problem (Sec. 1), the final point [24] of the gas spinodal is equal to  $Z = 3/2 Z_{\text{cr}}$ , and the spinodal can be approximated by a line segment. (Ideally, in infinite time, a fictitious particle (a pair) falls to the bottom due to friction, i.e., the orbit of this particle is circular, and thus one degree of freedom disappears. This means that the compressibility factor  $Z = 0.444$  at the point  $E_{\text{max}}^{\text{cr}}$  is reduced by the factor  $2/3$ , i.e.,  $Z_{\text{cr}} = 0.296$ .) This makes it

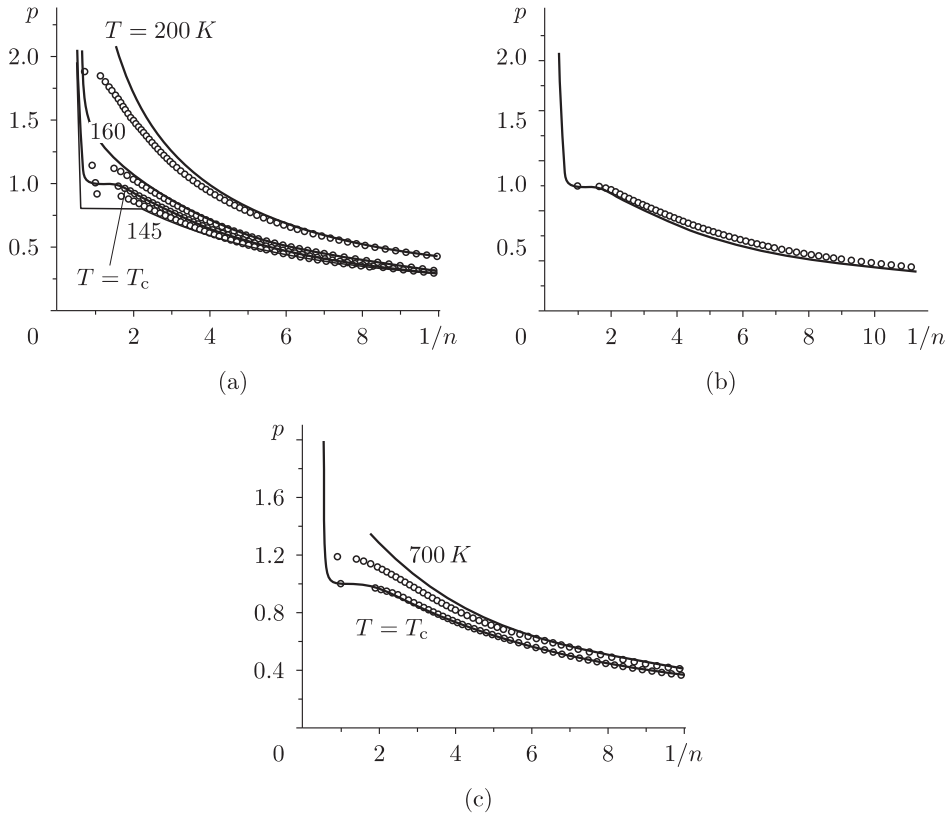


Figure 5: (a) Isotherms for argon. The continuous lines correspond to the experimental data, and the line formed by small circles is constructed according the isotherm of ideal Bose gas.

(b) Isotherms for water.  $Z_{\text{cr}} = 0.23$ .

(c) Critical isotherms for copper.  $Z_{\text{cr}} = 0.39$ .

The distribution of number theory, as opposed to the Bose–Einstein distribution (33), does not contain the volume  $V$ . Let us consider the distribution of number theory multiplied by unknown function  $\varphi_{\gamma_0}(V)$  which does not vary for  $\gamma \geq \gamma_0$  and  $T \leq T_{\text{cr}}$ . Then it follows from (36) that

$$P = \frac{\varphi'_{\gamma_0}(V) T^{\gamma_0+2}}{\Gamma(\gamma_0+2)} \int_0^\infty \frac{\varepsilon^{\gamma_0+1} d\varepsilon}{e^{-\kappa} e^\varepsilon - 1}, \quad \varphi'_{\gamma_0} = \frac{d\varphi_{\gamma_0}}{dV},$$

$$\varphi'_{\gamma_0}(V) \text{Li}_{\gamma_0+2}(y) = \frac{\rho}{T_B^{\gamma_0+1} \left(1 - \frac{\rho}{\rho_B}\right)^{\gamma_0+1}}, \quad \rho = \frac{R}{V}, \quad y = e^\kappa, \quad \kappa = \frac{\mu}{T}. \quad (37)$$

The differential equation for  $\varphi_{\gamma_0}$  is

$$\frac{V \varphi'_{\gamma_0}(V) \text{Li}_{\gamma_0+2}(y)}{\varphi_{\gamma_0}(V) \text{Li}_{\gamma_0+1}(y)} = 1, \quad V = \frac{R}{\rho}. \quad (38)$$

See Fig. 6.

possible to construct two points near  $P = 0$ ,  $Z = Z_{\text{cr}}$  by the theories of a new ideal (Bose) gas and by the fact that the chemical potential of the gas is equal to the chemical potential of an ideal liquid, and thus to approximately reconstruct the Zeno-line.



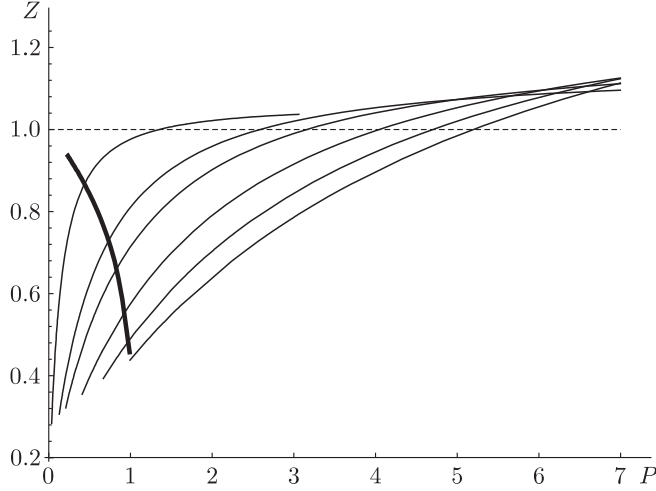


Figure 6: The dotted line shows the Zeno-line  $Z = 1$ . The bold line is the critical isotherm of an imperfect gas (argon) calculated theoretically; the thin lines correspond to the isochores of an imperfect gas for  $T < T_{\text{cr}}$ . Their initial points lie on the gas spinodal.

## 5 Ideal liquid

Let us now pass to the notion of ideal liquid. For an expert in mathematical physics, an ideal liquid is an incompressible liquid. In our mathematical conception of thermodynamics, we shall abide by this definition. In this case, on the Zeno-line on the plane  $\{P, Z\}$ , the point  $P(T, \rho)$  in (36) is uniquely defined for  $Z = 1$ . The isotherm  $T = \text{const}$  is a straight line. The second point is a point of the spinodal.

As is well known, the passage from the gaseous state to the liquid one is accompanied by the entropy drop. Naturally, the entropy, which determines the measure of chaotic behavior, is less for the liquid state than for the gaseous state. At the same time, the general property of “choosing” a subsystem with the greatest chaoticity among all possible subsystems leads to the property of constant entropy of the liquid, which was noted both theoretically and experimentally, even if the temperature tends to the absolute zero ([63], [64]) (the entropy tends to  $\log 2$ ).

In our model of ideal liquid as an incompressible liquid, we suppose in addition that the maximum of the entropy on a given isotherm (i.e., as  $\mu \rightarrow 0$ ) does not vary when the temperature varies (see below Section 6).

The big thermal potential is of the form

$$\Omega = -PV_\gamma = -\frac{\pi^{\gamma+1}V_\gamma T}{\Lambda^{2(1+\gamma)}} \frac{1}{\Gamma(2+\gamma)} \int_0^\infty \frac{t^{1+\gamma} dt}{(e^t/z) - 1} = \frac{-\pi^{\gamma+1}L^{2(1+\gamma)}T^{2+\gamma}}{\Lambda^{2(1+\gamma)}} \text{Li}_{2+\gamma}(z). \quad (39)$$

The entropy becomes

$$\begin{aligned} S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu} = (2+\gamma) \frac{L^{2(1+\gamma)}T^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \text{Li}_{2+\gamma}(z) - \frac{L^{2(1+\gamma)}T^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \text{Li}_{1+\gamma}(z) \frac{\mu}{T} \\ &= \frac{\pi^{\gamma+1}T^{1+\gamma}}{\Lambda^{2(1+\gamma)}} \left[ (2+\gamma) \text{Li}_{2+\gamma}(z) - \text{Li}_{1+\gamma}(z) \frac{\mu}{T} \right]. \end{aligned} \quad (40)$$

The maximum at  $\mu = 0$  is

$$S_{\mu=0} = \left(\frac{\pi}{\Lambda^2}\right)^{\gamma+1} (2+\gamma) \zeta(\gamma+2) T^{\gamma+1}. \quad (41)$$

We are interested in  $\gamma < 0$ .

Thus, we have two unknown constants, namely,  $\Lambda$  and the value of the entropy  $S_{\mu=0} = \text{const}$ . We define these two constants from the experimental value of the critical point of the liquid phase at the negative pressure (see Sec. 6 below), namely, from the minimum point of the pressure for a given simple liquid of the value  $\gamma$  at this point and from the temperature. This point is absent in the van der Waals model. This point is present in our model of liquid phase.

For example, for water, we obtain  $S_{\mu=0} = 3.495$  and  $\Lambda = 3.74$ . However, the computation is carried out under the assumption that the Zeno-line is a line segment, whereas this segment becomes curvilinear for water at low temperatures.

According to the van der Waals conception, we normalize as follows:

$$T^{\text{red}} = \frac{T}{T_{\text{cr}}}, \quad P^{\text{red}} = \frac{P}{P_{\text{cr}}}. \quad (42)$$

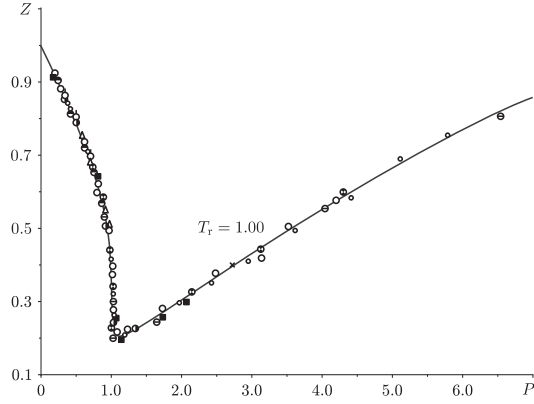


Figure 7: Experimental graph for the different gases, including for methane, ethylene, ethane, propane, *n*-butane, isopentane, *n*-heptane, nitrogen, carbon dioxide, and water. Each gas is equipped with a particular symbol on the graph.

Denote by  $\rho_0$  the solution of the equation

$$\frac{1}{T_B^{\text{red}}} + \frac{\rho}{\rho_B} = 1, \quad (43)$$

where  $T_B$  stands for the Boyle temperature and

$$T_B^{\text{red}} = \frac{T_B}{T_{\text{cr}}} \quad (44)$$

is a dimensionless quantity,  $T^{\text{red}} = \frac{T}{T_{\text{cr}}}$ . Then

$$\frac{\rho_0}{\rho_B} = 1 - \frac{1}{T_B^{\text{red}}}, \quad \rho_B^{\text{red}} = \frac{\rho_B}{\rho_0}. \quad (45)$$

Hence, the locus of the points of the quasi-ideal spinodals<sup>14</sup> is given by the formula

$$P^{\text{red}} = \frac{1}{\left(1 - \frac{1}{T_B^{\text{red}}}\right)} T^{\text{red}} \left(1 - \frac{T^{\text{red}}}{T_B^{\text{red}}}\right) Z(\gamma), \quad (46)$$

<sup>14</sup>That is, of the endpoints of the metastable state of the liquid phase.

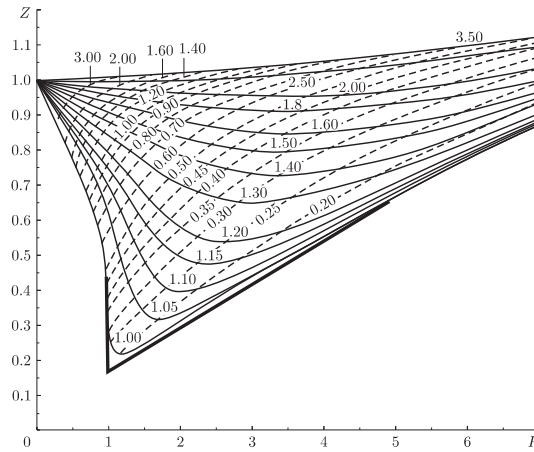


Figure 8: The continuous lines are the experimental isotherms for  $T \geq T_{\text{cr}}$  for methane, the dotted lines are experimental isochors. The theoretical critical isotherm coincides with the experimental isotherm up to  $Z = 0.29$  and is continued by a straight line up to the point  $P = 1$ ,  $Z = 1/\rho_0 = 0.14$  (see (27)–(29)). Further, at an acute angle, a tangent to the experimental isotherm at a point of Zeno-line is drawn. The straight line from the point  $P = 1$ ,  $Z = 0.14$  to the point of tangency is the critical isotherm of the ideal liquid phase. It can be seen by comparing the figure with Fig 7, the theoretical isotherm thus obtained corresponds to the isotherm of the “law of corresponding states” for the gases indicated in Fig. 7.

where  $\rho_B$  and  $T_B$  is the Boyle density and the Boyle temperature, respectively.

Here, for  $\gamma > 0$ ,

$$Z_{\text{cr}}^{\gamma(T^{\text{red}})} = \frac{\zeta(2 + \gamma(T^{\text{red}}))}{\zeta(1 + \gamma(T^{\text{red}}))}. \quad (47)$$

Let us recall that  $\gamma(T)$  can be calculated from the algebraic relation  $S_{\mu=0} = \text{const.}$

If we use the Maxwell condition, see Sec 5 (if Sec 6 is taken into account), which states that the transition from gas to liquid occurs for the same chemical potential, pressure, and temperature, then we can construct the so-called *binodal*. The binodal thus constructed coincides with the experimental one, in contrast to the van der Waals binodal (Fig. 4 (b)) and to the binodal presented in Fig. 3.

## 6 Wiener quantization of thermodynamics and a jump of critical exponents

The problem involving the so-called Maxwell rule for the transition “gas–liquid,” which is a natural complement of the new concept (of phenomenological thermodynamics) constructed above, is solved by using the tunnel (or Wiener) quantization introduced by the author already in his 1994 works; see [26] and [27] and also [28], [29], and [30]. We repeat here this quantization at a heuristic level.

We can say that the quantization of thermodynamics is simply called for. Indeed, we have the phase space<sup>15</sup> in which the momenta are the extensive quantities  $V$  and  $-S$ ,

<sup>15</sup>“A symplectic structure”.

and the corresponding coordinates are  $P$  and  $T$ . The usual quantization is of the form

$$\widehat{V} = ih \frac{\partial}{\partial P}, \quad -\widehat{S} = ih \frac{\partial}{\partial T}. \quad (48)$$

Just as in [31], let us invoke an analogy between the Schrödinger equation and the heat equation.

A. *The Schrödinger equation* corresponding to a noninteracting particle without an external field,

$$-ih \frac{\partial \psi}{\partial t} = (ih \nabla)^2 \psi. \quad (49)$$

The change of variables

$$\psi = e^{\frac{i}{\hbar} \mathbb{S}}$$

leads to the equation

$$\frac{\partial \mathbb{S}}{\partial t} + (\nabla \mathbb{S})^2 + ih \Delta \mathbb{S} = 0.$$

In this case, the quantization of the classical Hamilton–Jacobi equation consists in the addition of the term  $ih \Delta \mathbb{S}$ .

B. *The heat equation*

$$-\nu \frac{\partial u}{\partial t} = (\nu \nabla)^2 u, \quad (50)$$

$\nu$  is the kinematic viscosity. The change of variables

$$u = e^{-\frac{\mathbb{S}}{\nu}}$$

leads to the equation

$$\frac{\partial \mathbb{S}}{\partial t} + (\nabla \mathbb{S})^2 + \nu \Delta \mathbb{S} = 0. \quad (51)$$

The derivatives of this equation with respect to the coordinates are called the *Burgers equations*. In this case, the *Wiener quantization* consists in the addition of the viscous term.

*Remark 4.* In this special case, the Wiener quantization coincides with the Euclidean quantization well known in field theory. In the general case, it corresponds to the passage from the Feynman path integral to the Wiener path integral and is in essence presented in detail for physicists in the book [32].

In the Burgers equation, for  $p = \partial \mathbb{S} / \partial x$ , a shock wave occurs as  $\nu \rightarrow 0$ , i.e., a discontinuity of the  $\theta$ -function type, whereas, in thermodynamics, we have a jump of the  $\theta$ -function type for the transition “gas–liquid.” For the Burgers equation, the rule of “equal areas” arises. For the “gas–liquid” transition, the Maxwell rule of equal areas arises. In the heat equation, the Wiener quantization of energy yields  $\nu D_t$ , where  $D_t$  stands for the Heaviside operator,  $D_t = \frac{\partial}{\partial t}$ . In thermodynamics, the thermodynamical potential, the Gibbs energy, is equal to  $\mu N$ , where  $\mu$  stands for the chemical potential and  $N$  for the conjugate extensive quantity, the number of particles. Hence,

$$\widehat{N} = \nu \frac{\partial}{\partial \mu},$$

and the role of time<sup>16</sup> is played by  $\log -\mu$ , because, under this quantization, the operator  $\nu \mu (\partial / \partial \mu)$  corresponds to the Gibbs energy.

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<sup>16</sup>Cf. Matsubara Green function, where the role of the imaginary time is played by the parameter  $\beta = 1/T$  [65].

For us, the one-dimensional case  $p_1 = V$  and  $q_1 = P$  is of importance. In the general case, the focal point (the point of inflection [34], [35]) is of the form  $q \sim p^3$ , i.e.,

$$P_{\text{cr}} \sim (V - V_{\text{cr}})^3 = \left( \frac{\rho_{\text{cr}} - \rho}{\rho \rho_{\text{cr}}} R \right)^3, \quad (52)$$

which corresponds to the classical critical index (the exponent) equal to three. The asymptotic solution (as  $\nu \rightarrow 0$ ) of (51) corresponding to this point is expressed by the Weber function. The critical point itself corresponds to the point  $x = 0$ .

The Weber function is of the form

$$u(x) \cong \frac{1}{\sqrt{\nu}} \int_0^\infty e^{-\frac{x\xi - \xi^4}{\nu}} d\xi. \quad (53)$$

If we set  $x = 0$ , then the change of variables

$$\xi = \sqrt[4]{\nu} y^{1/4}$$

gives a singularity as  $\nu \rightarrow 0$  of the order of  $\nu^{-1/4}$ . What does it mean, from the classical point of view and classical measurement, for the case in which the condition referred to in [20] as the “semiclassical condition” holds (this means that we are outside the focal point)? For the Laplace transform, this means that we are in a domain in which the Laplace asymptotic method is applicable, i.e., in a domain for which

$$\Psi(x) = \frac{1}{\sqrt{\nu}} \int_0^\infty e^{-\frac{px - \tilde{S}(p)}{\nu}} dp, \quad \lim_{p \rightarrow 0} \frac{\tilde{S}(p)}{p^4} < \infty, \quad \tilde{S}^{(4)}(p)|_{p=0} \neq 0. \quad (54)$$

The solution  $p_\nu(x)$  of the Burgers equation can be evaluated by the formula

$$p_\nu(x) = \nu \frac{\partial \log u(x)}{\partial x} = \frac{\int_0^\infty \exp\left\{\frac{-x\xi - \tilde{S}(\xi)}{\nu}\right\} \xi d\xi}{\int_0^\infty \exp\left\{\frac{-x\xi - \tilde{S}(\xi)}{\nu}\right\} d\xi}. \quad (55)$$

After the substitution

$$\frac{\xi}{\sqrt[4]{\nu}} = y,$$

as  $x \rightarrow 0$  we obtain

$$p_\nu(x) \rightarrow_{x \rightarrow 0} \sqrt[4]{\nu} \cdot \text{const.} \quad (56)$$

In our case, the momentum  $p_\nu(x)$  is the volume  $V$ .

If the solution of the relation

$$x = \partial \tilde{S} / \partial p$$

is nondegenerate, i.e.,

$$\frac{\partial^2 \tilde{S}}{\partial p^2} \neq 0$$

at the point

$$\frac{\partial \tilde{S}}{\partial p} = x,$$

then in this case, the reduced integral (55) is bounded as  $\nu \rightarrow 0$ . For this integral to have a singularity of order  $\nu^{1/4}$ , we must apply to this integral the fractional derivative

$D^{-1/4}$  with respect to  $x$ . The value of  $D^{-1/4}$  at the function equal to one,  $D^{-1/4}1$ , gives approximately  $x^{1/4}$ .

In our case, the pressure  $P$  plays the role of  $x$ , and the volume  $V$  plays the role of momentum  $p$ . Therefore,  $V \sim P^{1/4}$ , i.e.,

$$P_{\text{cr}} \sim (V - V_{\text{cr}})^4 \sim \left( \frac{\rho - \rho_{\text{cr}}}{\rho \rho_{\text{cr}}} R \right)^4.$$

Following M. Green [36], D. Yu. Ivanov, a deep experimenter, poses the following question: Why are the deviations from the classical theory in the critical opalescence observed within the limits of hundredths of a degree from the critical points, whereas the deviations in thermodynamical properties show [7] a nonclassical behavior at a much larger distance from the critical point?. Professor Ivanov claims that rather many questions of this kind have been accumulated (see, for example, [8]), and all these questions mainly deal with the behavior of practical systems. The point is that, from the point of view of the developed theory of critical indices [6], there must be a drastic passage to the classical indices outside a neighborhood of the critical point.

To make Ivanov's question understandable for persons who are not experts in critical points, we paraphrase the question for the case of geometric optics, when the sun rays are collected by a magnifying glass to a focus. If we had created the special construction for the vicinity of the focus in which the paper smoulders, then the experimenter could ask why the experiment gives a smooth picture of transition in the double logarithmic coordinates and the indices are preserved far away from the smouldering small vicinity of the focus. In the present case, the smouldering paper can be compared with the small area of opalescence (drastic fluctuations near the critical point) for which a separate theory was constructed. At the same time, the special function defining the point within the wave theory (like the Weber function) can be continued quite smoothly to a much wider domain in which the paper does not smoulder. In the opinion of Ivanov, this fact is much more important than the fact that Wilson's theory gives the index 4.82 rather than 4.3, which is given by modern experiments.

Can the experimental index 4.3 be explained in principle in the framework of the conception presented by the author?

Whereas in classical mechanics there is no dependence on the Planck constant  $\hbar$ , in classical thermodynamics there is a slow dependence of the viscosity on  $T$  and  $\rho$ , and thus *vice versa* as well. In our picture, the "stretching" of  $P_{\text{cr}}$  and  $T_{\text{cr}}$  in the experiment for real gases (Figs. 7 and 8) is greater than in the van der Waals model, which enables us to introduce in the "stretching" the parameter  $\nu^\varepsilon$  (i.e.,  $P = \nu^\varepsilon V^3$ ) and obtain the index  $\delta = 4.3$  for  $\varepsilon = 0.07$ . Thus, in principle, the answer can be "yes."

It follows from what was said above that new critical indices arise only due to quantization of the conjugate pairs  $\{P, V\}$  and  $\{T, S\}$ . Thus, the relationships between intensive quantities can be taken classical, because everything is carried out under the assumption of infinitely small viscosity. In this case, one can also pass to another coordinates, to the pressure and density.

Write, as usual,

$$p = \frac{P - P_{\text{cr}}}{P_{\text{cr}}}, \quad \theta = \frac{T - T_{\text{cr}}}{T_{\text{cr}}}, \quad v = \frac{\rho - \rho_{\text{cr}}}{\rho_{\text{cr}}}.$$

In the classical case, we have ([37], p. 344)

$$p \sim v^3, \quad v \sim \theta^{1/2}, \quad \theta \sim v^2.$$

In the classical case, we obtain

$$p \sim \theta^{3/2}.$$

In the tunnel quantum case, we obtain  $\beta = 0.375$  (cf. [37], p. 356) in the limit as  $\nu \rightarrow 0$ , and thus not precisely (the stretching is not taken into account). This is obtained for the van der Waals model quantized in the tunnel way.

An important specific feature of Wiener quantization is that, at the expense of viscosity, it smoothes the acute angle on the graphs 8 and 9, and thus removes the discrepancy between the theory and the experiment.

The heuristic role of viscosity when penetrating through the barrier is described in Sec. 2. As is well known, an exponential penetration through the barrier occurs in the standard quantization as well. However, in the Wiener quantization, we restrict ourselves to a power-law approximation (see Sec. 6 below).

If  $\nu > 0$ , then an uncertainty principle arises. Let us proceed with the consideration of this principle.

Thus, in the case of Wiener quantization, the main operators are not the momentum operator  $i\hbar \frac{\partial}{\partial x}$  and the operator of multiplication by  $x$ , but the Heaviside operator  $\nu D = \nu \frac{\partial}{\partial x}$  and the operator of multiplication by  $x$ . The constant  $\nu$  was determined in [38] as viscosity. In contrast to the Plank constant, the constant  $\nu$  can smoothly depend on the variables of the system. The main distinction of the tunnel quantization from the Euclidean and usual quantization is that it is considered up to  $O(\nu^k)$ , where  $k$  is any fixed number, i.e., it is factorized in  $O(\nu^k)$ .

But first it is necessary to define the space where these operators act.

As is well known, the Heaviside operator is related to the two-sided Laplace transform. This was shown already by van der Pol and Bremmer in [39]. Introduce a family of functions  $\varphi(p)$  to which we shall apply the two-sided Laplace transform, namely,

$$\varphi(p) = \int_0^\infty e^{-p^2 \xi} \Xi(\xi) d\xi, \quad (57)$$

and thus these functions themselves are one-sided Laplace transforms,

$$F_\lambda \Xi(\xi) = \int_0^\infty e^{-\lambda \xi} \Xi(\xi) d\xi,$$

for  $\lambda = p^2$ . Denote by  $F_\lambda^\pm$  the two-sided Laplace transform,

$$F_\lambda^\pm \varphi(p) = \int_{-\infty}^\infty e^{-\lambda p} \varphi(p) dp.$$

If the functions  $\Xi(\xi)$  are compactly supported and infinitely differentiable, then the closure of the operator  $\nu D$  with respect to this domain can be carried out in the Bergman space. Then the functions  $\Psi(x) = F_x^\pm \varphi(p)$  here become analogous to the  $\Psi$ -functions in the Schrödinger quantization. Moreover,  $\Psi^*(x) = \Psi(x)$ , because these functions are real-valued.

Let us note first of all that the squared function or, equivalently, the squared dispersion  $\Delta \hat{f}$  of the operator  $\hat{f}$  is

$$(\Delta \hat{f})^2 = |(\hat{f} - \bar{f})^2|,$$

and, since  $\hat{f}$  is not selfadjoint, the function  $(\hat{f} - \bar{f})^2$  need not be positive, and hence one must pass to its absolute value. Therefore, the corresponding theorem for generic operators fails to hold in general. However, for the operators  $\nu D$  and  $x$  on a reduced

function space, we obtain  $|\Delta\nu D||\Delta x| \geq \nu/2$ . It can readily be seen that Weyl's proof (which is presented in the comments to §16 of Chap. II in [20]) can easily be transferred to the operators  $\nu D$  and  $x$  in the above function space.

Let us note some consequences of tunnel (or Wiener) quantization for the “quantum” Bose gas.

A specific feature of photon gas, which is mentioned in [9], §§ 62,63, is that the number of particles in this gas,  $N$ , is a variable quantity (rather than a given constant, which is the case for ordinary gas).

Thus, since the number of particles  $N$  in thermodynamics is conjugate to the chemical potential, it follows that, if the number of particles is undefined, then the chemical potential can be given precisely,  $\mu = 0$ , under the assumption that  $\mu$  and  $N$  are tunnel quantized and the uncertainty principle holds.

A contradiction between the conception of the author and the conception of physicists going back to Einstein is also removed. In the case of a gas for which  $N$  is fixed, we have

$$\sum_{i=0}^{\infty} N_i = N \quad (58)$$

according to the relation in [9], and the chemical potential  $\mu$  can be a small positive quantity. This is obvious, because  $N_i \leq N$ ; however, this contradicts Einstein's original conception claiming that  $\mu \leq 0$ . This contradiction is removed if the relationship of the uncertainty principle holds for  $\mu$  and  $N$ , because, if  $\mu = 0$ , then  $N$  can take infinite values as well, and therefore the case  $\mu > 0$  is impossible.

Thus, it can be said that both the scaling hypothesis and the hypothesis of tunnel quantization do not agree near the critical point with the old thermodynamical conception of the four potentials. However, the hypothesis of tunnel quantization does not contradict the conception of the four potentials, namely, the hypothesis complements the conception, and this works not only near the critical point but also on the entire domain “gas–liquid” by agreeing with the Maxwell rule and by removing logical discrepancies in Bose gas theory.

We have explained Wiener quantization, which enabled us to remove some problems. Let us now also explain the second quantization. The principal element in Fock's approach is the indistinguishability of particles. In our theory, it follows from the original axiom. Although there are no natural Hilbert spaces here, in contrast to quantum mechanics, we can still obtain correct distinguished representations and limits as  $\hbar \rightarrow 0$  (see [40], Chap. 1, Appendix 1.A) and then, in view of the indistinguishability of particles, perform the second quantization of classical theory by introducing the creation and annihilation operators. Certainly, this is possible only under the condition of the *principle of indistinguishability of particles in our measurements*, which follows from the main axiom, rather than from the “identity principle” introduced in [20].

In classical mechanics, such operators were introduced in [41] and [42] on the basis of the Schönberg concept (see [43] and [44]).

Thus, the contemporary derivation of the Vlasov equation is obtained by applying the method of second quantization for classical particles [40]. In this case, as  $N \rightarrow \infty$ , one obtains a system for which the creation and annihilation operators asymptotically



commute,

$$\begin{aligned}
\dot{u}(p, q, t) &= \left( \frac{\partial U}{\partial q} \frac{\partial}{\partial p} - p \frac{\partial}{\partial q} \right) u(p, q, t) \\
&\quad + \int dp' dq' v(p', q', t) \left( \frac{\partial V(q, q')}{\partial q} \frac{\partial}{\partial p} + \frac{\partial V(q, q')}{\partial q'} \frac{\partial}{\partial p'} \right) u(p', q', t) u(p, q, t), \\
\dot{v}(p, q, t) &= \left( \frac{\partial U}{\partial q} \frac{\partial}{\partial p} - p \frac{\partial}{\partial q} \right) v(p, q, t) \\
&\quad + \int dp' dq' u(p', q', t) \left( \frac{\partial V(q, q')}{\partial q} \frac{\partial}{\partial p} + \frac{\partial V(q, q')}{\partial q'} \frac{\partial}{\partial p'} \right) v(p', q', t) v(p, q, t),
\end{aligned} \tag{59}$$

where  $U(q_i)$  is an external field and  $V(q_i, q_j)$  is the pairwise interaction.

If one replaces  $u$  and  $v$  by the operators of creation and annihilation  $\hat{u}$  and  $\hat{v}$  in the Fock space, then, after this change, system (59) becomes equivalent to the  $N$ -particle problem for the Newton system.

However, according to the mathematical proof, this can happen only for the case in which the classical particles are indistinguishable (from the point of view of the main axiom).

Only in this case the projection from the Fock space to the  $3N$ -dimensional space of  $N$  particles gives *precisely* the system of Newton equations.

Note that the substitution

$$u(p, q, t) = \sqrt{\rho(p, q, t)} e^{i\pi(p, q, t)}, \quad v(p, q, t) = \sqrt{\rho(p, q, t)} e^{-i\pi(p, q, t)}, \tag{60}$$

reduces system (59) to the form

$$\begin{aligned}
\dot{\rho}(p, q, t) &= \left( \frac{\partial W^t}{\partial q} \frac{\partial}{\partial p} - p \frac{\partial}{\partial q} \right) \rho(p, q, t), \\
\dot{\pi}(p, q, t) &= \left( \frac{\partial W^t}{\partial q} \frac{\partial}{\partial p} - p \frac{\partial}{\partial q} \right) \pi(p, q, t) + \int dp' dq' \frac{\partial V(q, q')}{\partial q'} \frac{\partial \pi(p', q', t)}{\partial p'} \rho(p', q', t);
\end{aligned} \tag{61}$$

we have here

$$W^t(q) = U(q) + \int dq' V(q, q') \rho(p', q', t) dp' dq'.$$

The first equation of system (45) is the *Vlasov* equation (see [56]), where  $\rho$  stands for the distribution function and  $W^t(q)$  for the dressed potential (see Sec. 2, formulas (5)ff.); the other equation is linear, and its meaning is discussed in [59].

Note further a tunnel-quantum jump of the index at the points of the spinodal of the liquid phase. The classical index of the spinodal is equal to 2, namely,  $P \sim V^2$ , similarly to turning points in quantum mechanics. The Airy function corresponds to it. Similarly to (52)–(54), we obtain

$$\Psi(x) = \frac{1}{\sqrt{\nu}} \int_0^\infty e^{-\frac{px - \tilde{S}(p)}{\nu}} dp, \quad \lim_{p \rightarrow 0} \frac{\tilde{S}(p)}{p^3} < \infty, \quad \tilde{S}^{(3)}(p)|_{p=0} \neq 0. \tag{62}$$

The solution  $p_\nu(x)$  of the Burgers equation can be evaluated by the formula (53). As  $x \rightarrow 0$ , after the change  $\frac{x}{\sqrt[3]{\nu}} = y$ , we obtain

$$p_\nu(x) \rightarrow_{x \rightarrow 0} \sqrt[3]{\nu} \cdot \text{const.} \tag{63}$$

In our case, the momentum  $p_\nu(x)$  is the volume  $V$ . Hence, similarly to the consideration between the formulas (55) and (56), we obtain  $P \sim V^3$ , and the index at the points of the spinodal becomes equal to three.

*Remark 5.* It is possible that an experimenter, when considering the approaching of the critical isotherm for  $T > T_{\text{cr}}$  to the critical point  $\mu = 0$ , moves (due to the indeterminacy principle) towards increasing values of  $N$ , and hence towards increasing density, and arrives at the spinodal of the liquid phase. This effect is similar to the accumulation of the wave crest which overturns afterwards (a part of the particles outruns the point of creation of the shock wave). In this case, the critical index 4.3 passes to the index 3 of the spinodal (and this index occasionally coincides with the classical index of the critical point). This passage, which is described by the Vlasov equation, was experimentally noticed in [8] and in other works. Therefore, the experiments of Ivanov [8] and Wagner ([57], [58]), where the modifications of the critical index  $\delta$  from 4.3 to 3 were obtained when approaching the critical point, do not contradict our conception.

For the creation of dimers, the author of the present paper used the creation and annihilation operators for pairs of particles and referred to it as the ultrasecond quantization [30]. Experimenters do not distinguish between dimers either, counting only their number (for example, as showed by Calo [45], the presence of 5–7% dimers leads to the appearance of a cluster cascade).

Thus, we discover new relations, namely an extension of the program “partitio numerorum” in number theory, from the point of view of the notion of Hartley entropy, and indicate possible generalizations of quantization, which lead to an extension of the Heisenberg indeterminacy principle [25].

Ultrasecond quantization leads to thermodynamics in nanocapillaries and enabled us to obtain the superfluidity of liquids in nanotubes [46]–[48], which was confirmed in experiments (see [49]–[51]).

## 7 Negative pressure and a new critical point of possible transition from liquid to “foam”

First, we use the Wiener quantization of thermodynamics to explain why, in Sec. 5, the model of incompressible liquid was used to derive the condition  $S|_{\mu=0} = \text{const}$ , where the constant is independent of the temperature.

Because of the Bachinskii relation on the Zeno line, the incompressible liquid model leads to a rigid relation between the density (concentration)  $\rho$  and the temperature. Since the value of  $N$  is undefined for  $\mu = 0$  (i.e., the concentration  $\rho$  is undefined), the temperature is also undefined, and hence, according to the indeterminacy principle, the entropy takes a constant value and can be determined. (In addition, we note that, for  $\mu = 0$ , the activity is equal to 1 at any (undefined) temperature). This precisely means that  $S|_{\mu=0} = \text{const}$ . As we shall see below, the value of this constant is uniquely determined by the new critical point at which the liquid passes into “foam” (dispersion state). The value of this point also determines the constant  $\Lambda$  in the definition of  $\Omega$ , and hence, after calculating  $\varphi_\gamma(V/V_{\text{cr}})$ , it is possible to obtain the complete description of the distribution function for the gas branch in thermodynamics. We note that the indeterminacy at the spinodal point agrees with the results of experiments on the absolute instability of the spinodal point, which were performed by academician Skripov and his school.

Now we pass to negative  $Z$ .

As is known, the Bose–Einstein distribution is obtained as the sum of terms of an infinitely decreasing geometric progression. If the progression is bounded by the number

$N$ , then the potential is of the form

$$\Omega = -T \sum_k \log \left( \frac{1 - \exp \frac{\mu - \varepsilon_k}{T} N}{1 - \exp \frac{\mu - \varepsilon_k}{T}} \right). \quad (64)$$

What is the relationship<sup>17</sup> between  $E_i$  and  $\gamma$ ?

1) Ultrarelativistic case.  $E = cp$ . Here

$$E_{i+1} - E_i = \int_{E_i}^{E_{i+1}} cp p^2 dp = \frac{1}{4} \left( p^4(E_{i+1}) - p^4(E_i) \right) \sim \frac{3}{4} cp^3(E_i^{i+1}) = \frac{3}{c^2} (E_i^{i+1})^3. \quad (65)$$

2) Nonrelativistic case.  $E = \frac{p^2}{2m}$ . Here

$$\begin{aligned} E_{i+1} - E_i &= \int_{E_i}^{E_{i+1}} \frac{p^2}{2m} p^2 dp = \frac{1}{2m} \left( \frac{p^5}{5}(E_{i+1}) - \frac{p^5}{5}(E_i) \right) \\ &= \frac{1}{2m} \left( \frac{(\sqrt{2mE_{i+1}})^5}{5} - \frac{(\sqrt{2mE_i})^5}{5} \right) \cong \text{const}(E_i^{i+1})^{3/2}. \end{aligned} \quad (66)$$

3) Consideration of the degrees of freedom.  $E = \frac{p^{2+\sigma}}{2mp_0}$ . Here

$$E_{i+1} - E_i = \int_{E_i}^{E_{i+1}} \frac{p^{2+\sigma}}{2m} p^2 dp \cong \text{const}(E_i^{i+1})^{(4+\sigma)/(2+\sigma)}. \quad (67)$$

By (31),  $\gamma = (1 - \sigma)/(2 + \sigma)$ , and thus  $\gamma < 0$  for  $\sigma > 1$ .

As was proved in [17]–[18], passing to the limit in the Euler–Maclaurin formula, we obtain

$$N = \frac{1}{(\gamma + 1)\Gamma(\gamma + 1)} \int_0^\infty \left\{ \frac{1}{e^{b\xi} - 1} - \frac{N}{e^{Nb\xi} - 1} \right\} d\xi^\alpha. \quad (68)$$

In particular, for  $\gamma = -1/2$ ,

$$N = \frac{1}{\Gamma(3/2)} \int_0^\infty \left\{ \frac{1}{e^{b\xi^2} - 1} - \frac{N}{e^{Nb\xi^2} - 1} \right\} d\xi. \quad (69)$$

The absolute value of the derivative of the integrand can readily be estimated by using the identities presented below. By the Euler–Maclaurin bounds, this shows that one can pass from the sums of the form (57) to the corresponding integrals with the accuracy needed here.

Hence, denoting  $N_{\text{cr}} = k_0$ , we obtain the following formula for the integral at  $\mu = 0$ :

$$\mathcal{E} = \frac{1}{\alpha\Gamma(\gamma + 2)} \int \frac{\xi d\xi^\alpha}{e^{b\xi} - 1} = \frac{1}{b^{1+\alpha}} \int_0^\infty \frac{\eta d\eta^\alpha}{e^\eta - 1}, \quad (70)$$

where  $\alpha = \gamma + 1$ . This implies that

$$b = \frac{1}{\mathcal{E}^{1/(1+\alpha)}} \left( \frac{1}{\alpha\Gamma(\gamma + 2)} \int_0^\infty \frac{\xi d\xi^\alpha}{e^\xi - 1} \right)^{1/(1+\alpha)}. \quad (71)$$

---

<sup>17</sup>The physicists who are not interested in Euler–Maclaurin-type bounds used to pass from sums to integrals can skip the following scheme of the proof of these bounds.

We obtain

$$\begin{aligned} \int_0^\infty \left\{ \frac{1}{e^{b\xi} - 1} - \frac{k_0}{e^{k_0 b \xi} - 1} \right\} d\xi^\alpha &= \frac{1}{b^\alpha} \int_0^\infty \left( \frac{1}{e^\xi - 1} - \frac{1}{\xi} \right) d\xi^\alpha \\ &+ \frac{1}{b^\alpha} \int_0^\infty \left( \frac{1}{\xi} - \frac{1}{\xi(1 + (k_0/2)\xi)} \right) d\xi^\alpha - \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{k_0^\alpha}{e^{k_0 \xi} - 1} - \frac{k_0^\alpha}{k_0 \xi(1 + (k_0/2)\xi)} \right\} d\xi^\alpha. \end{aligned} \quad (72)$$

Write

$$c = \int_0^\infty \left( \frac{1}{\xi} - \frac{1}{e^\xi - 1} \right) \xi^\gamma d\xi.$$

After the change  $k_0 \xi = \eta$ , we obtain

$$\begin{aligned} \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{k_0^\alpha}{e^\eta - 1} - \frac{k_0^\alpha}{\eta(1 + \eta/2)} \right\} d\xi^\alpha &= \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{1}{e^\eta - 1} - \frac{1}{\eta(1 + \eta/2)} \right\} d\eta^\alpha \\ &= \frac{k_0^{1-\alpha}}{b^\alpha} \left\{ \int_0^\infty \left( \frac{1}{e^\eta - 1} - \frac{1}{\eta} \right) + \int_0^\infty \frac{d\eta^\alpha}{2(1 + \frac{\eta}{2})} \right\} = -c \frac{k_0^{1-\alpha}}{b^\alpha} + c_1 \frac{k_0^{1-\alpha}}{b^\alpha}. \end{aligned} \quad (73)$$

Since  $\frac{1}{\eta(1+\eta/2)} = \frac{1}{\eta} - \frac{1}{2(1+\eta/2)}$ , after denoting  $c_1 = \int_0^\infty \frac{d\eta^\alpha}{2(1+\frac{\eta}{2})}$ , we can write

$$\int_0^\infty \left( \frac{1}{\xi} - \frac{1}{\xi(1 + \frac{k_0}{2}\xi)} \right) d\xi^\alpha = \frac{k_0}{2} \int_0^\infty \frac{d\xi^\alpha}{1 + \frac{k_0}{2}\xi} = \left( \frac{k_0}{2} \right)^{1-\alpha} \int_0^\infty \frac{d\eta^\alpha}{1 + \eta} = c_1 \left( \frac{k_0}{2} \right)^{1-\alpha}. \quad (74)$$

Hence,

$$\begin{aligned} -\frac{1}{b^\alpha} c_1 + \frac{1}{b^\alpha} c \left( \frac{k_0}{2} \right)^{1-\alpha} - \frac{k_0^{1-\alpha}}{b^\alpha} \int_0^\infty \left\{ \frac{1}{e^\eta - 1} - \frac{1}{\eta(1 + \frac{\eta}{2})} \right\} d\eta^\alpha - \frac{1}{2} \int \frac{d\eta^\alpha}{1 + \frac{\eta}{2}} \cdot \frac{k_0^{1-\alpha}}{b^\alpha} \\ = -\frac{1}{b^\alpha} c + \frac{k_0^{1-\alpha}}{b^\alpha} c. \end{aligned} \quad (75)$$

Since  $k_0$  is the number of particles,  $b = 1/T$ , and  $\alpha = 1 + \gamma$ , it follows that  $k_0 b^\alpha$  for  $\gamma > 0$  is the value of the Riemann zeta function,  $\zeta(1 + \gamma)$ . Therefore,  $k_0^{\gamma+1}$  increases for  $\gamma < 1$ , and the first term of the right-hand side of equation (75) can be neglected. Introducing the function

$$\mathcal{M}(\gamma + 1) = (c(\gamma)/\Gamma(\gamma + 1))^{1/(1+\gamma)}, \quad (76)$$

we see that the compressibility factor  $Z_\gamma = -\zeta(\gamma+2)/\mathcal{M}(\gamma+1)$  is subjected to a flexion<sup>18</sup> from  $\gamma > 0$  to  $\gamma < 0$ .

In this case, we obtain another critical point, which fully corresponds to the physical meaning (see [53]).

Thus, if the compressibility factor is negative, then we divide  $\mathcal{E}/N$  by  $T^{\gamma+1}$  with  $\gamma < 0$  rather than by  $T$ , because

$$\frac{\mathcal{E}}{N} \Big|_{\mu=0} = \frac{\zeta(\gamma+2) T_{\text{red}}^{\gamma+2}}{\mathcal{M}(\gamma+1) T_{\text{red}}} = T_{\text{red}}^{\gamma+1} \frac{\zeta(\gamma+2)}{\mathcal{M}(\gamma+1)},$$

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<sup>18</sup>Since the ‘‘Young moduli’’ for the compression and extension are distinct, a flexion of the spinodal occurs.

i.e., the energy evaluated for a single particle at  $\mu = 0$  (at the “degeneration” point), for  $P < 0$ , is proportional to  $T_{\text{red}}^{\gamma+1}$ , i.e., to the temperature taken to a power with an exponent less than one. For  $P < 0$ , the compressibility factor becomes a dimensional quantity; however, this is always considered in this very way on curves in the space  $\{Z, P\}$  when using the van der Waals normalization (26).

We write

$$F(\xi) = \left( \frac{1}{\xi} - \frac{1}{e^\xi - 1} \right).$$

For  $\gamma < 0$  and  $\mu = 0$  we have

$$N_c = \sum_{j=1}^{\infty} \frac{j^\gamma}{e^{bj} - 1} = \sum_{j=1}^{\infty} j^\gamma \frac{1}{bj} - \sum_{j=1}^{\infty} j^\gamma F(bj). \quad (77)$$

Since the function  $f(x) = x^\gamma F(bx)$  decreases monotonically, we have

$$\sum_{j=1}^{\infty} j^\gamma F(bj) = \sum_{j=1}^{\infty} f(j) \leq \int_0^{\infty} f(x) dx = \int_0^{\infty} x^\gamma F(bx) dx = b^{-\gamma-1} \int_0^{\infty} x^\gamma F(x) dx \quad (78)$$

(the Nazaikinskii inequality).

Thus, the spinodal point  $\gamma(T)$  is determined by the relation

$$N = b^{-1} \zeta(1 - \gamma) + O(b^{-1-\gamma}), \quad \gamma < 0, \quad b = \frac{1}{T_r},$$

where  $\zeta$  is the Riemann zeta function.

For the critical isotherm we have  $T_r = 1$ . Hence  $\gamma(T) = -\gamma_0$ . For the point  $T_r$  and the isochor  $T_r^{\gamma_0+1} \zeta(\gamma_0 + 1)$  we obtain the relation for  $\gamma(T_r)$  from the equation

$$T_r^{\gamma_0+1} \zeta(\gamma_0 + 1) = T_r \zeta(1 + |\gamma(T_r)|). \quad (79)$$

The less  $T_r$ , the greater  $|\gamma(T)|$ . But  $\gamma(T)$  cannot exceed 1, because the pressure and  $Z$  become  $-\infty$  at this point.

The negative pressure at the point of the spinodal of liquid phase (for  $\tilde{\mu} = 0$ ) is equal to  $-T^{2+\gamma(T)} \zeta(2 + \gamma(T_r))$ , where the value of  $\gamma(T)$  obtained above is negative. The condition  $\gamma(T) \leq 1$  bounds the transition region for the temperature

$$T_r^{\gamma_0} \leq \frac{\zeta(2)}{\zeta(\gamma_0 + 1)} = \frac{\pi^2}{6\zeta(\gamma_0 + 1)}. \quad (80)$$

For a model we can consider thick rubber with many small slots (see Appendix in [33], which is almost incompressible in compression, and because of the holes-slots, has a small Young modulus in tension. It is natural to consider tension of a liquid as the appearance of nanoholds, i.e., of negative energy  $PV$ , which can be treated as negative pressure (pressure of the holes).

Let us now present a graph Fig. 9 for negative pressure for the Lennard–Jones potential, where the new critical point is obtained by using a computer experiment<sup>19</sup>.

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<sup>19</sup>The absolute zero of temperature is inaccessible. This is visually seen in the logarithmic scale of temperatures  $\log T_{\text{red}}$ , where the absolute zero corresponds to  $-\infty$ .

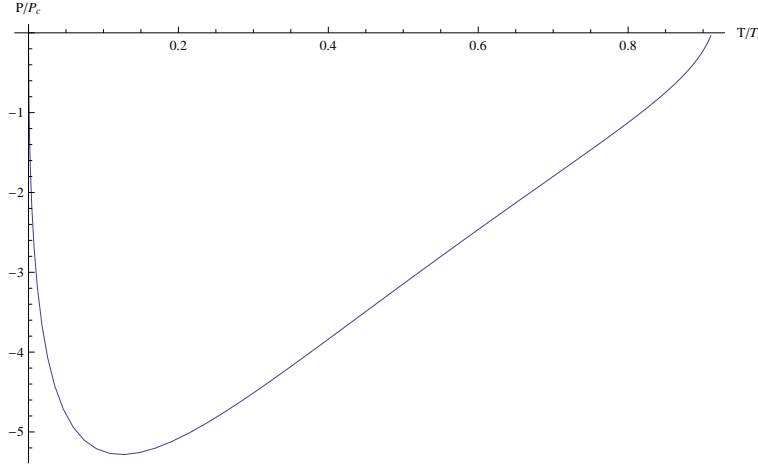


Figure 9: The spinodal in the coordinates given by the temperature  $T_{\text{red}}$  and the negative pressure  $P_{\text{red}}$ .

## 8 On Homogeneous Mixtures of Gases

When considering a gas mixture, we would like to attract the attention at the following fundamental point. As is well known, in statistical physics and thermodynamics, the energy is sometimes connected with the number of degrees of freedom and the temperature; for example, this is the case in the equidistribution law. It turns out in this case that the energy depends on the temperature and on the number of degrees of freedom and does not depend on the mass. The sequential usage of this conception gave us a continuous parameter  $\gamma$  related to the fractal dimension in the momentum space. Continuing the use of this conception in the case of a mixture of pure gases, we should speak of concentration rather than on density, i.e., we should neglect the masses of miscible pure gases.

The sequential application of number theory in thermodynamics, i.e., the consideration of the main axiom for the gas mixture (which was in fact made by experimenters, at least in the case of air (see [55])), leads to the formulas presented below.

If two values  $\mathcal{E}_1$  and  $\mathcal{E}_2$  expanded into sums of  $N_1$  and  $N_2$  summands, respectively, correspond to the fractional dimensions  $\gamma_1$  and  $\gamma_2$ , respectively, and the values of the pairs  $\{\mathcal{E}_1, N_1\}$  and  $\{\mathcal{E}_2, N_2\}$  are on the “verge of degeneration,” i.e., adding an excessive number to  $N_1$  and to  $N_2$  leads to the “appearance of the Bose condensate,” then, for the sum  $\mathcal{E}_1 + \mathcal{E}_2$  and for  $N_1 + N_2$ , any adding of an excessive number to  $N_1 + N_2$  also leads to the “appearance of the Bose condensate.”

Let  $\rho_1^{\text{cr}}$  and  $\rho_2^{\text{cr}}$  be the critical concentrations ((in the units  $\text{cm}^{-3}$ )), and let  $N_1$  and  $N_2$  be proportional to the molar concentrations,

$$N_1/(N_1 + N_2) = \alpha, \quad (81)$$

$$N_2/(N_1 + N_2) = \beta, \quad (82)$$

$$N = N_1 + N_2, \quad \alpha + \beta = 1. \quad (83)$$

Since

$$\mathcal{E}_{\text{cr}} = \mathcal{E}|_{\mu=0} = N|_{\mu=0} Z^{\text{cr}} \frac{\Gamma(\gamma + 1)}{\Gamma(\gamma + 2)} T^{\text{cr}} = N^{\text{cr}} Z^{\text{cr}} (\gamma^{\text{cr}} + 1)$$

for  $\gamma > 0$ , it follows that, dividing the equation

$$\mathcal{E}_{\mu=0}^{\text{sum}} = \mathcal{E}_{\mu=0}^{(1)} + \mathcal{E}_{\mu=0}^{(2)} = N_1^{\text{cr}} (\gamma_1 + 1) Z_1^{\text{cr}} T_1^{\text{cr}} + N_2^{\text{cr}} (\gamma_2 + 1) Z_2^{\text{cr}} T_2^{\text{cr}}$$

by  $N_{\text{sum}}^{\text{cr}}$ , we obtain the relation <sup>20</sup>

$$(\gamma_{\text{sum}}^{\text{cr}} + 1)Z_{\text{sum}}^{\text{cr}}T_{\text{sum}}^{\text{cr}} = \alpha(\gamma_1^{\text{cr}} + 1)Z_1^{\text{cr}}T_1^{\text{cr}} + \beta(\gamma_2^{\text{cr}} + 1)Z_2^{\text{cr}}T_2^{\text{cr}}, \quad (84)$$

where  $Z^{\text{cr}} = \zeta(\gamma + 2)/\zeta(\gamma + 1)$ , the subscripts 1 and 2 refer to the first and second gas of the mixture, and the subscript sum refers to the gas mixture. Similarly,

$$S = N(Z - \mu/T),$$

and, using the additivity of the entropy and dividing by  $N_{\mu=0}^{\text{sum}}$ , we obtain the relation

$$Z_{\text{sum}}^{\text{cr}}(\gamma_{\text{sum}}^{\text{cr}} + 2) = \alpha(\gamma_1^{\text{cr}} + 2)Z_1^{\text{cr}} + \beta(\gamma_2^{\text{cr}} + 2)Z_2^{\text{cr}}. \quad (85)$$

It follows from the above two relations that the quantity  $\gamma = \gamma_{\text{sum}}$  almost linearly depends also on the values  $\alpha$  and  $T_{\text{cr}} = T_{\text{cr}}^{\text{sum}}$ . This fact is well known as ‘‘Kay’s rule’’ in the phenomenological theory of mixtures. For air, we have  $T_{\text{cr}}^{\text{sum}} = 232 \text{ K}$ , whereas  $T_{\text{cr}} = 255 \text{ K}$  for oxygen (20% in air) and  $T_{\text{cr}} = 226 \text{ K}$  for nitrogen (80% in air). The value of  $T_{\text{cr}}^{\text{sum}}$  coincides with the value of this quantity evaluated according to the above formulas up to the accuracy of 0.5%.

He have defined  $Z_{\text{cr}}$  for ideal gases, and hence also  $\gamma_{\text{cr}}$  for gas mixtures. For a mixture of real gases, we must define the function  $\varphi_{\gamma}^{\text{mix}}$ .

It turns out that, for such mixtures, the Zeno-line is not a segment of a straight line, which is the case and is observed experimentally for pure gases. Therefore, for a mixture, it is not sufficient to find the values  $T_B^{\text{mix}}$  and  $\rho_B^{\text{mix}}$ . One must also define the function  $\varphi_{\gamma_{\text{cr}}}^{\text{mix}}$ . This can be carried out by using the following formulas.

We are interested only in the values of  $\mu_1$  and  $\mu_2$  that correspond to the Zeno-line of each of the gases (see (4)-(38)).

Since, by assumption, the critical point belongs to the domain of homogeneity, it follows that the concentrations  $\alpha$  and  $\beta$  are preserved, and hence, using equations (61)–(63), we obtain the following equation for the sum of the entropies, where  $\kappa = \mu/T$ :

$$\begin{aligned} & (\gamma_{\text{sum}} + 2)Z_{\gamma_{\text{sum}}+2}(e^{\kappa_{\text{sum}}}) - \kappa_{\text{sum}} \\ &= \alpha\{(\gamma_1 + 2)Z_{\gamma_1+2}(e^{\kappa_1}) - \kappa_1\} + \beta\{(\gamma_2 + 2)Z_{\gamma_2+2}(e^{\kappa_2}) - \kappa_2\}, \end{aligned} \quad (86)$$

where  $Z_{\gamma+2}$  is equal to the ratio  $\text{Li}_{\gamma+2}(e^{\kappa})/\text{Li}_{\gamma+1}(e^{\kappa})$ .

Recall that the values of  $\kappa_1$  and  $\kappa_2$  are taken according to the Zeno-lines of the first and the second gas, respectively. Hence, using the given values of  $\gamma$ ,  $\gamma_1$ , and  $\gamma_2$  obtained from (81), we find the value  $\kappa = \kappa_{\text{sum}}$ , which defines the function  $\varphi_{\gamma}(V)$  by the relation (38). This enables us to define the dependence of  $T_{\text{cr}}^{\text{sum}}$  for a mixture of real gases.

## 9 Scheme for the evaluation of the percentage for the concentration of a mixture of two gases in a liquid

For the liquid phase, we consider the quasi-ideal case of incompressible liquid. Then, for the sum of entropies, we obtain the relation

$$\begin{aligned} T^{\gamma+1}\{ \text{Li}_{\gamma+2}(e^{\kappa})(\gamma + 2) - \kappa \text{Li}_{\gamma+1}(e^{\kappa}) \} &= T_1^{\gamma_1+1}\{ \text{Li}_{\gamma_1+2}(e^{\kappa_1})(\gamma_1 + 2) - \kappa_1 \text{Li}_{\gamma_1+1}(e^{\kappa_1}) \} + \\ &+ T_2^{\gamma_2+1}\{ \text{Li}_{\gamma_2+2}(e^{\kappa_2})(\gamma_2 + 2) - \kappa_2 \text{Li}_{\gamma_2+1}(e^{\kappa_2}) \}. \end{aligned} \quad (87)$$

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<sup>20</sup>The full energy does not depend on the masses of the particles, as well as in the theory of Brownian particles (see [38]). The latter theory can be expressed in terms of the Wiener path integral, which is equal to the Feynman path integral with imaginary Planck constant. This is an additional argument in favor of the Wiener quantization.

We assume that the state is an equilibrium, i.e., the temperature of the elements of the mixture is equal. Then we have

$$T_1 = T_2 = T.$$

If we assume that the full NT-internal energy  $\mathcal{E}$  of each of the components is preserved, then we obtain

$$\begin{aligned} S &= \frac{T^{\gamma+2} \text{Li}_{\gamma+2}(e^\kappa)(\gamma+1)}{T} + T^{\gamma+1} \{ \text{Li}_{\gamma+2}(e^\kappa) - \kappa \text{Li}_{\gamma+1}(e^\kappa) \} \\ &= \frac{\mathcal{E}}{T} + T^{\gamma+1} \{ \text{Li}_{\gamma+2}(e^\kappa) - \kappa \text{Li}_{\gamma+1}(e^\kappa) \}. \end{aligned} \quad (88)$$

The derivative with respect to  $\kappa$  of the second term in the expression (84) is equal to the derivative of  $\text{Li}_{\gamma+1}(e^\kappa)$  with respect to  $\kappa$ .

This means that, integrating over all  $\gamma$  and taking the variation of (83), we obtain the condition of chemical equilibrium,

$$\mu \delta N = \mu_1 \delta N_1 + \mu_2 \delta N_2. \quad (89)$$

This implies a relationship between the chemical potentials, as in the law of mass action. A similar formula holds for a mixture of a greater number of components.

Let us now consider a small correlation sphere for the liquid state of a homogeneous mixture of pure substances (as a rule, these are 6–8 molecules) and consider all possible replacements of molecules of the gas 1 and the gas 2 in this sphere. Let us form an analog of stoichiometric coefficients, as if these were “chemical bonds.”

Now using the relations for chemical potentials, we obtain a system of necessarily many equations for the original molecules, as it happens for the law of mass action for the original atoms. This enables us to define the mean concentration of each of these two gases in the liquid phase.

*Remark 6.* Note that it is not rigorously proved in the cycle of papers of the author that to any “pure” gas there corresponds a Zeno-line. As is known, for example, the ideal line is substantially curved for water under low densities. Water (the creation of dew), as well as mercury, must be excluded from our theory of real gases and their mixtures. We have heuristically obtained the Zeno-line only for the Lennard–Jones interaction potential. The same heuristic proof can be carried out for other interaction potentials. Therefore, one can agree that, for pure gases interacting according to the same potential, the Zeno-line is approximately a line segment (and this segment is not quite straight in the problem in Sec. 1).

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